PREPARATION OF LANTHANIDE COMPLEXES IN ACETONITRILE

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by

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I would like to dedicate this work to my wife.

Contents

CHAPTER THREE

Reactions of the Lanthanide Metals (La, Nd, Eu and Tm) with the Hexafluorides (UF_6, MoF_6 and WF_6) in MeCN

CHAPTER FOUR

Reactions between the Lanthanide Metals (La, Nd, Eu and Tm) and the Nitrosonium Compounds, $NOUF_6$, $NOMoF_6$, $NOPF_6$, $NOBF_4$ and $NOWF_7$ in MeCN

CHAPTER FIVE

Reactions of Pyridine (py) and Trimethylamine (NMe_3) with $[Ln(NCMe)_3][MF_x]_3$ (Ln=La, Nd or Eu; M=Mo or W; x= 6 or 7) or $NOPF_6$ in Acetonitrile

SUMMARY

The reactions of the lanthanide metals (La, Nd, Eu and Tm) with the high oxidation state fluorides (UF_6, MoF_6 and WF_6) in acetonitrile and the reactions between these four lanthanide metals and the NO^+ compounds ($NOWF_7$, $NOBF_4$, $NOUF_6$, $NOMoF_6$ and $NOPF_6$) in acetonitrile are described in this thesis. Some reactions between the acetonitrile solvated lanthanide compounds produced from the oxidation of the lanthanide metals by MoF_6 or WF_6 and the simple N-donor ligands are also described. These simple ligands are pyridine and trimethylamine which are regarded as weak ligands.

The solvated salts $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6\}_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6 or 7) have been prepared from the oxidation of the lanthanide metals by the hexafluorides of tungsten or molybdenum in acetonitrile. These salts are all pale yellow in colour and very prone to hydrolysis. The apparent coordination number of the Ln(III) cations in the complexes is 3, which is low compared with most lanthanide complexes. The reason for this is suggested to be interaction between the Ln(III) cation and the fluoroanions.

Uranium hexafluoride is reported to be the strongest oxidizing agent among the three high oxidation state fluorides used in this study. There is, however, no evidence of any reaction occurring between the metals, lanthanum, neodymium, europium and thulium and UF_6. Polymerization of acetonitrile and reduction of

UF_6 takes place instead. Molybdenum hexafluoride reacts with europium metal or bright pieces of neodymium ingot freshly cut in the dry glove box. It does not, however, react with lanthanum, thulium and neodymium powder metals. Tungsten hexafluoride reacts with europium and lanthanum metals which are the most reactive among four lanthanide metals used in this work. All the reactions observed in this work are very slow and occur to a limited extent, therefore, the yields are all rather small. The reactions of the lanthanide metals with the hexafluorides used in the present work are similar to many "d" block elements of the periodic table. It is proposed that the oxide film on the surface of the lanthanide metals plays an important role in the oxidation of the metals, which inhibits their reactions, especially in the case of UF_6.

The salt $NOPF_6$ reacts with all metals used, $NOBF_4$ reacts only with europium and $NOMoF_6$ reacts only with neodymium, however, $NOUF_6$ and $NOWF_7$ do not react with any of the metals. A number of possible causes for the differences in NO^+ salt behaviour are discussed.

The compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$, and $[Eu(NCMe)_3][WF_x]_3$ (x= 6 or 7) react readily with pyridine or trimethylamine in acetonitrile at room temperature to form the insoluble compounds:

$[La(py)_7(NCMe)][WF_x]_3$, $[Nd(py)_7(NCMe)][MoF_6]_3$

$[Eu(py)_7(NCMe)][MoF_6]_3$, $[Eu(py)_7(NCMe)][WF_x]_3$

$[La(NMe_3)_4(NCMe)_2][WF_x]_3$, $[Nd(NMe_3)_4(NCMe)_2][MoF_6]_3$

$[Eu(NMe_3)_4(NCMe)_2][MoF_6]_3$, $[Eu(NMe_3)_4(NCMe)_2][WF_x]_3$

x= 6 or 7.

The reactions between $NOPF_6$ and pyridine, or trimethylamine in acetonitrile result in the formation of two solids. Their microanalyses reveal that they are the adducts, $NOPF_6 \cdot 2py$ and $NOPF_6 \cdot 2NMe_3$.

CHAPTER ONE

INTRODUCTION

1:1 General Properties of Lanthanide Elements[1,2,3]

The lanthanide elements are also known as "rare earths". They are the largest naturally occurring group in the Periodic Table. According to the definition of the international union of pure and applied chemistry, they include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, as well as the elements Sc and Y. Because they are identical in their chemical and physical properties, some of them exist together in individual minerals and they are difficult to separate. Lanthanide elements are divided into two groups on the basis of their separability, one is the "light earths" or the "cerium group" (La to about Eu), the other is the "heavy earths" or the "yttrium group" (Gd to Lu plus Y and Sc).

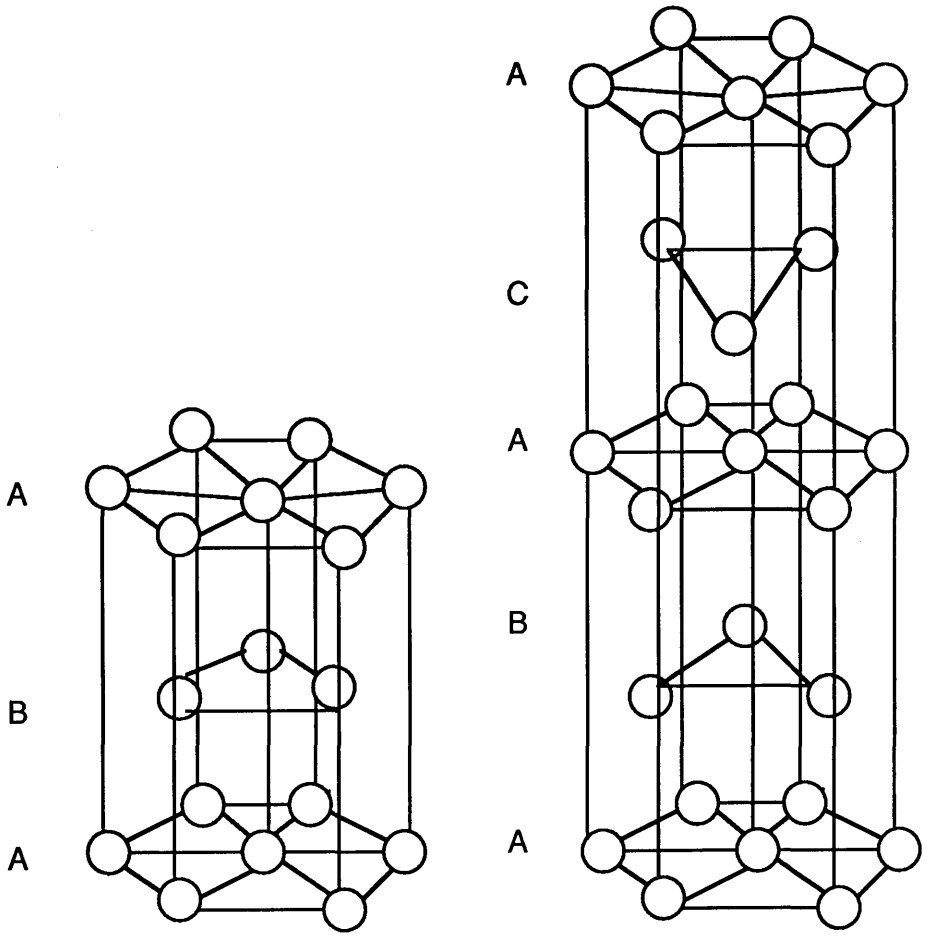
The lanthanide contraction affects significantly the properties of the third transition series. The lanthanide contraction consists of a steady decrease in the radii of their atoms and ions along the group. The reason for the decrease is due to the imperfect shielding of one electron by another in the same subshell. From La to Lu, the number of 4f electrons and nuclear charge increases one by one, but owing to the shapes of the orbitals, the shielding of one 4f electron by another is imperfect, so that the effective nuclear charge increases as the number of 4f electrons increases, thus causing a reduction of $4f^n$ shell. The accumulation of these effects forms the total lanthanide contraction.

The lanthanide metals are silvery in appearance and rather

soft, but gradually become hard across the series. In common with many of the transition elements, most of the lanthanide metals and their compounds are strongly paramagnetic, that is, they tend to align themselves parallel to a magnetic field. The measurement of the magnetic susceptibility of a lanthanide compound can give a accurate assessment of its oxidation state.

The lanthanide elements are rather electropositive and reactive metals. They generate stable compounds with the elements, H, C, N, O, and the halides. On the other hand, their reactivity depends significantly on the radius of the atom, thus europium, Eu is the most reactive among the lanthanide metals because it has the largest metal radius. Although their reactions are usually less vigorous, practically they can react with most of the non-metals if heated. They react slowly with cold water, but rapidly on heating, and dissolve readily in dilute acids, even when cold, to give aqueous solution of Ln(III) salts.

Among the four lanthanide metals used in the present work, La, Nd and Eu belong to the "light earths" and Tm belongs to the "heavy earths". Although lanthanum possesses no f electron, it is still thought of as one of the lanthanide elements and it is more naturally abundant than lead. Metallic lanthanum is prepared by the quantitative conversion of the oxide to the fluoride and then, the reduction of the fluoride by Ca metal. The crystal structure of the lanthanum metal at the room temperature is known to be double-c hexagonal close-packed (Fig.1.1). Lanthanum is covered with a light blue oxide film in dry air, protecting it from further



(a) The normal hexagonal close-packed(hcp) structure.
(b) The double C-axis hexagonal close packed(dhcp) structure.

Fig. 1.1 Crystal structures of the La, Nd and Tm.

oxidation and it gradually becomes covered with a white hydrated oxide in humid air. The metal radius of lanthanum is the third largest among all of the lanthanide metals and, so it is also reactive. Metallic lanthanum oxidizes slowly, but continuously in air. Neodymium is roughly the same as lanthanum in abundance and its preparation method is similar to that of lanthanum. The crystal structure of the neodymium metal at room temperature is a double-c hexagonal close-packed (Fig. 1.1). In air metallic neodymium is oxidized to a lesser degree than lanthanum. In air a thin gray film covers the surface, inhibiting further oxidation. The crystal structure of the europium metal at room temperature is known to be body centred cubic. In this case, each atom has 8 nearest neighbours situated at 4.5827 Å . Europium has a silver metallic lustre, but quickly gains a yellowish tint. Metallic europium can be cut with a knife or razor blade; it is almost as soft as lead. Europium which has the largest metal radius among all of the lanthanide elements, is the most reactive. Metallic europium energetically reacts with humid air at room temperature, forming a yellow chemical compound [$Eu(OH)_2 \cdot H_2O$], which turns white after a period of time. Metallic europium reacts violently with cold water, releasing hydrogen and forming a yellow compound which dissolves easily in water. Thulium is one of the "heavy earths". The abundance of thulium in igneous rocks is about 0.3 g/tonne. The crystal structure of the thulium at room temperature is known to be hexagonal closed-packed (Fig. 1.1). Thulium is less reactive than lanthanum, neodymium and europium. In compounds, thulium is trivalent. The four lanthanide metals used in the present work were stored in a

nitrogen gas glove box. Some of their physical properties are summarized in Table 1.1.

1:2 Some Thermodynamic Aspects of Lanthanide Chemistry[4]

One of the main features in lanthanide chemistry is the variation of oxidation state. From a thermodynamic standpoint, the relative stabilities of oxidation states are the result of the interplay of ionization energies with lattice and hydration energies.

For lanthanide elements, the occurrence of unusual oxidation states has been studied for a long time, but their occurrence is discussed mainly in terms of the stability of the empty, half-filled and filled shell configurations. In addition, stability seems to increase gradually as the number of f electrons rises towards these stable configurations. For example, $Eu^{2+}(aq)$ has the configuration $[Xe]4f^7$, its stability is at a maximum because of its half-filled shell. Correspondingly, $Sm^{2+}(aq)$ also has a good stability since it is near a half-filled shell configuration, namely $[Xe]4f^6$. The $Yb^{2+}(aq)$, $[Xe]4f^{14}$, and $Tm^{2+}(aq)$, $[Xe]4f^{13}$ cations are similar. However, from this point of view, the stabilities of the dipositive lanthanides in the second half of the series should follow the order.

$$Dy^{II} < Ho^{II} < Er^{II} < Tm^{II} < Yb^{II}$$

Table 1.1
Some Physical Properties of La, Nd, Eu and Tm

	La	Nd	Eu	Tm
Atomic number	57	60	63	69
Atomic weight (mg/gmol $^{-1}$)	138.91	144.24	151.96	168.93
Crystal structure	dhcp	dhcp	bcc	hcp
Atomic radii (Å)	1.8791	1.8214	2.0418	1.7462
Atomic volume (cm ^{3} /mol)	22.602	20.583	28.979	18.124
Lattice constants (Å)	a_o 3.7740 c_o 12.171	a_o 3.6582 c_o 11.797	4.5827	a_o 3.5375 c_o 5.5540
Principal oxidation number	+3	+3	+2,+3	+3
Density (g/cm ^{3} , 240 ^{o}C)	6.146	7.008	5.244	9.321
Melting point (^{o}C)	918	1021	822	1545
Boiling point (^{o}C)	3464	3070	1529	1950
Electronic configuration	$5d6s^2$	$4f^4 6s^2$	$4f^7 6s^2$	$4f^{13} 6s^2$
Ionic radii (Å , M^{3+})	1.17	1.12	1.09	1.02
Ionization energy (Ei/ev)	M^+ 5.577 M^{2+} 11.06 M^{3+} 19.175	M^+ 5.49 M^{2+} 10.72 M^{3+} 22.14	M^+ 5.67 M^{2+} 11.25 M^{3+} 24.92	M^+ 6.18 M^{2+} 12.05 M^{3+} 23.68
Electrode potential E(V)	-2.17	-2.32	-1.99	-2.31

The dihalide of dysprosium has been known for a long time, but until now, the holmium and erbium dihalides have not been synthesized. Therefore, this explanation is not perfect and should be modified.

From the spectroscopic data on lanthanide compounds, the crystal field splittings are only about 2-3% of the values in the corresponding transition metal complex. This shows that in lanthanides, the 4f orbitals are buried in the xenon core where they interact only weakly with ligand electrons. This is a significant difference between lanthanides and d block transition ions. On the other hand, because of the well-known lanthanide contraction, the radii of ions of the same charge decrease quite steadily across the series. The relative stability of the dipositive aqueous ions across the series can be discussed below from the standpoint of thermodynamics.

For the reaction:

$$M^{2+}(aq) + H^{+}(aq) = M^{3+}(aq) + 1/2H_2(g) \qquad [1\text{-}1]$$

$$\Delta G^{o}m = FE^{o}(M^{3+}/M^{2+}),$$
$$\Delta G^{o}_{m} = \Delta H^{o}_{m} - T\Delta S^{o}_{m} \qquad (1\text{-}1)$$

Where ΔG^{o}_{m} is the standard free energy change of the reaction [1-1], $E^{o}(M^{3+}/M^{2+})$ is the standard potential of the reaction, ΔH^{o}_{m} is the standard enthalpy of the reaction, ΔS^{o}_{m} is the standard entropy change and T is the temperature, F is the

Faraday constant.

By means of the thermodynamic cycle for the process [1-1]:

$$M^{2+}(aq) + H^{+}(aq) \xrightarrow{\Delta H^{o}_{m}} M^{3+}(aq) + 1/2H_2(g)$$

$$\downarrow -\Delta H^{o}_{h}(M^{2+}, g) \qquad \uparrow \Delta H^{o}_{h}(M^{3+}, g)$$

$$M^{2+}(g) + H^{+}(aq) \xrightarrow{I_3 + \Delta H^{o}_{H}} M^{3+}(g) + 1/2H_2(g)$$

$$\Delta H^{o}_{m} = I_3 + \Delta H^{o}_{H} - \Delta H^{o}_{h}(M^{2+},g) + \Delta H^{o}_{h}(M^{3+},g) \qquad (1\text{-}2)$$

From (1-1) and (1-2):

$$\Delta G^{o}_{m}=I_3+\Delta H^{o}_{h}(M^{3+},g) - \Delta H^{o}_{h}(M^{2+},g)-T\Delta S^{o}_{m} + \Delta H^{o}_{H} \qquad (1\text{-}3)$$

where the I_3 is the third ionization energy, $\Delta H^{o}_{h}(M^{3+},g)$ and $\Delta H^{o}_{h}(M^{2+},g)$ are the hydration enthalpies of $M^{3+}(g)$ and $M^{2+}(g)$, respectively. ΔH^{o}_{H} is the standard enthalpy of the reaction [1-2]:

$$H^{+}(aq) + e^{-}(g) \rightleftharpoons 1/2H_2(g) \qquad [1\text{-}2]$$

Assuming that ΔS^{o}_{m} as well as ΔH^{o}_{H} is constant,

$$\Delta G^{o}_{m} = I_3 + \Delta H^{o}_{h}(M^{3+}, g) - \Delta H^{o}_{h}(M^{2+}, g) + C \qquad (1\text{-}4)$$

where C is a constant.

Although there are some difference in the change tendencies of ΔG^{o}_{m} and I_3 of the first transition series, due to the irregularities in $\Delta H^{o}_{h}(M^{3+},g)$ and $\Delta H^{o}_{h}(M^{2+},g)$, the variations of ΔG^{o}_{m} and I_3 are still similar. These irregularities are due to the ligand field effects which are very small in the case of lanthanides. Since the radii of M^{2+} and M^{3+} ions decrease smoothly across the series, the values of $\Delta H^{o}_{h}(M^{3+},g)$ and $\Delta H^{o}_{h}(M^{2+},g)$ are expected to change smoothly with atomic number. Therefore, the changes of ΔG^{o}_{m} and I_3 of the lanthanides should be very close. Because the I_3 values of the lanthanides follow the order:[4]

La < Ce < Pr < Nd < Pm < Sm < Eu » Gd < Tb < Dy > Ho > Er < Tm < Yb

there is the same sequence in the ΔG^{o}_{m} of the lanthanides, thus for dipositive aqueous ions of lanthanides, their stabilities are in the order:

La < Ce < Pr < Nd < Pm < Sm < Eu » Gd < Tb < Dy > Ho > Er < Tm < Yb

At present, the only well-characterized aqueous dipositive ions are $Eu^{2+}(aq)$, $Sm^{2+}(aq)$ and $Yb^{2+}(aq)$. This is in agreement with the sequence above. According to the redox potentials, $Eu^{2+}(aq)$ is more stable than $Sm^{2+}(aq)$. Obviously, the unknown dipositive aqueous ions should be even more unstable than those already known to exist.

The sequence of the stabilities of the tetrapositive oxidation states can be obtained in a similar fashion:

Ce > Pr > Nd > Pm > Eu > Gd « Tb > Dy > Ho

The experimental facts correspond with this sequence. For example, Ce, Pr, and Tb tetrafluorides have been obtained, but for Pm to Gd, and Ho to Lu inclusive, the compounds of the +4 oxidation state have not yet been adequately characterized.

1:3 Coordination Chemistry of the Lanthanides

(1) Classical Inorganic Complexes of the Lanthanides

Most of the classical compounds of the lanthanides are often regarded as simple or double salts, or when containing water, as hydrated salts. However, in most cases they are complex compounds. Lanthanides are hard acids as defined by Pearson[5]. Therefore, it is not surprising that many inorganic complexes, especially those isolated from aqueous solutions, contain oxygen-donor ligands.

In the case of other donor ligands, as there is a competition between these ligands and water molecules, an aqua complex forms. Thus, the complex compounds of inorganic non-oxygen ligands of lanthanides are very limited and most of them only form monodentate complex compounds. Lanthanide halides have been studied extensively in solution. Fluorides of the lanthanides are particular examples of non-oxygen donor ligand complexes, because the fluoride ions compete effectively with water

molecules and enter the primary coordination sphere of the cation in aqueous solutions. The stoichiometries of the precipitated fluorides indicate that they are almost anhydrous while the other lanthanide halides prepared from aqueous solution normally contain 6-9 water molecules.[6] Some of the typical halogen- and oxygen- donor ligands encountered in inorganic lanthanide complex compounds are given in Table 1.2.

The number of oxygen-donor ligands is large as seen from Table 1.2. Also, because some of these anions may undergo condensation reactions in solution, the number and variety of the types of complexes formed are greatly increased. For example, the selenite ion in aqueous solution is at equilibrium with the hydrogenselenite and diselenite ions and different compounds may be precipitated.

Apart from classical inorganic complex compounds of the lanthanides, many lanthanide complexes which have organic ligands have been obtained from aqueous solution. As most of the organic ligands are polydentate, the lanthanide complex compounds containing these ligands are more stable. Also, lanthanide complexes with oxygen-donor organic ligands are more numerous than those with nitrogen-donor ligands probably because the former ligands are more often negatively charged, a clear advantage when forming essentially ionic bonds. However, by using polar organic solvents, in order to avoid competitive coordination by water, complexes with organic ligands such as ethylenediamine(en), dien, 2',2'-bipyridyl(bipy), and

Table 1.2
Typical Ligands in Classical
Inorganic Complexes of Lanthanides

ligand type	example
X	F^- , Cl^- , Br^- , I^-
XH	OH^-
XH_2	OH_2
XO_2	NO_2^-
XO_3	CO_3^{2-} , NO_3^- , SO_3^{2-} , SeO_3^{2-} , BrO_3^-
XO_4	VO_4^{3-} , NbO_4^{3-} , CrO_4^{2-} , MoO_4^{2-} WO_4^{2-} , PO_4^{3-} , SO_4^{2-} , ClO_4^- , SeO_4^{2-}

terpyridyl(terpy) can be prepared.

(2) Coordination Numbers of the Lanthanide Complexes

Typical coordination numbers of the lanthanide complexes are 7, 8, 9 and 10 which have been shown by X-ray diffraction data of many lanthanide complexes.[7] It is especially noteworthy that coordination numbers are normally more than six, and six is unusual. This is significantly different from d-block transition metal chemistry. There is no directional covalent bonding in the lanthanide complexes and there are generally considerable ionic radii of the lanthanides. However, five, four, and even three coordination numbers are known in a few cases. The very high coordination number of twelve is obtained by chelate anions which have their donor atoms close together, such as NO_3^-.

The distribution of the coordination compounds of the lanthanides, excluding the organolanthanides, versus coordination number has been worked out by Palenik[8], which is given in Table1.3.

Table 1.3
The Distribution of the Coordination Compounds of the Lanthanides, as a Function of Coordination Number (CN)

CN	3	4	5	6	7	8	9	10	11	12
Number	4	1	1	19	20	62	70	23	4	7

The preponderance of structures with coordination number of 8 or 9 illustrates the preference of the lanthanides for these two coordination numbers. In fact, the $Ln(H_2O)_9^{3+}$ ion is well-known for the elements La to Yb. If 8 and 9 are regarded as usual coordination numbers for lanthanide complexes, those lanthanide complexes with coordination number of 3 to 5 are abnormal. Steric effects are regarded as the primary consideration for synthesizing complexes with a low coordination number. Most of the reported lanthanide complexes with a coordination number of 3, 4, or 5 involve the trimethylsilylazide(tmsa) ligand,[9-12] for example, $Nd(tmsa)_3$ and $Eu(tmsa)_3$.

1:4 Classification of Lanthanide Complex Compounds

In 1965, the complex compounds of the lanthanides were classified according to four types by T. Moeller et.al,[13] ion-pair associations, isolable adducts, chelates and miscellaneous. In 1981, A. D. Garnovskii, V. T. Panyushkin and T. V. Gritsenko classified the complex compounds according to three types, namely, molecular adducts of salts of lanthanide cations and ligands, inner complexes, and organometallic compounds.[14] The definition of these three types of complex compounds of the lanthanides are described below.

(1) Molecular Complexes

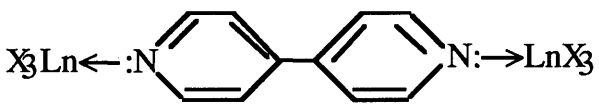
They are adducts of salts and other derivatives of lanthanides

with inorganic, organic, and organometallic ligands, in which the ligand system is completely preserved, that is, they have the general formulas $mLnX_3 \cdot nL$ and $mLnX_3 \cdot nL \cdot pSolv.$, where Ln is a lanthanide; X denotes the anion of the salt; L is a ligand; Solv. is the solvent; and m, n, p are the numbers of molecules of the respective components appearing in the adduct. This type of complex compound of the lanthanides includes numerous complex compounds containing oxygen, nitrogen, phosphorus, and other heteroatoms, as well as unsaturated bonds, as donor centres. Some examples of the molecular complexes of lanthanides are given in Table 1.4. Complexes of the lanthanides containing di- and multidentate ligands occupied a very important place among the molecular complexes of lanthanides. Numerous molecular complexes of the lanthanides are those containing di- and multidentate ligands. According to the number of donor atoms in the ligand, the situation of these donor atoms participating in coordination with the metal, and their relative arrangement, the molecular complexes may again be divided into two types: one is acyclic complexes and the other is metal chelates. The former complexes form with both all monodentate ligands and di- and multidentate ligands systems, however, in the cases of di- and multidentate ligands, the realization of metal-containing rings is still difficult (I). The latter complexes form with di- and multidentate ligands whose spatial orientation of the donor centres promotes the realization of metal-containing rings, i.e., metal chelate (II).

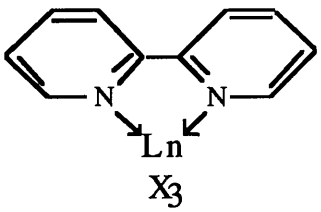
Table 1.4

Molecular Complexes of the Lanthanides

Ligand	Composition of Complex	Ref.
Urea	$Ln(CH_3COO)_3L_3 \cdot 1,5H_2O$ (Ln=La-Sm)	15
Ethanol	$LnCl_3L_2 \cdot H_2O$ (Ln=La, Ce)	16
Benzo-15-crown-5	$Ln(NO_3)_3 \cdot L$ (Ln=La-Sm)	17
Dipropionamide	$Ln(ClO_4)_3 \cdot L_4$ (Ln=Y, La-Yb)	18
2-picoline-N-oxide	$Ln(NCS)_3 \cdot L_n$ (Ln=La-Lu, n=3-5)	19
4-Aminoantipyrine	$Ln(ClO_4)_3L_6$ (Ln=Y, La, Pr, Nd, Sm, Gd, Dy)	20
Dimethyl sulfoxide	$Ln(PF_6)_3L_n$ (Ln=y, La-Lu; 7≤ n≤ 7.5)	21
Tetramethylene sulfoxide	$LnI_3L_n \cdot mH_2O$ (Ln=Y, La-Lu; n=5,7,8; m=0,3)	22
Tribenzylarsine oxide	$Ln(NO_3)_3L_3$ (Ln=Y, La-Yb)	23
Hexamethylphosph-oramide	$Ln(ClO_4)_3 \cdot L_6$ (Ln=Y, La-Lu)	24
2-benzylamino-4-benzyliminopent-2-ene	$Ln(NO_3)_3L_3$ (Ln=La,Pr,Nd,Sm,Gd,Dy,Er,Yb)	25



(I)



(II)

(2) Organometallic Derivatives of Lanthanides

These derivatives are complexes with σ M-C bonds and π complexes of the lanthanides.[26,27] The cyclopentadienyl, cycloindenyl, cycloheptatrienyl, and cyclooctatetraene derivatives of the lanthanides are those which have been studied most thoroughly.[14] Many organometallic complexes of the lanthanides have been listed in the published reviews[26,27] and in a monograph.[28]

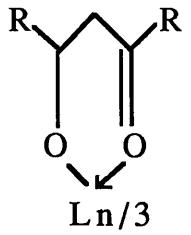
(3) Inner Complexes

The inner complexes are classified as a separate type because they, unlike the molecular metal chelates, have metal-containing rings with a deprotonated ligand system.[29,30] Some of these lanthanide complexes are listed in Table 1.5. The lanthanide complexes of ß-diketones (III), 8-hydroxyquinoline (IV), and O-hydroxyazomethines (V)[14] are examples of inner complexes.

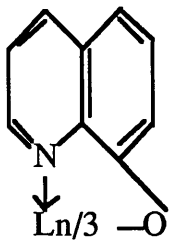
Table 1.5

Inner Complexes of the Lanthanides

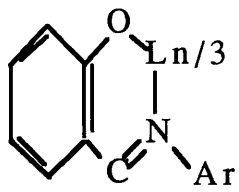
Ligand	Composition of complex	Ref.
Formic acid	LnL_3 (Ln=Ce-Gd)	31
Tartaric acid (H_4L)	$Ln_4L_3\ nH_2O$ (Ln=Pr,Nd,Sm,Gd,Tb,Dy,Ho,E; n=12,13,14	32
Methylsalicyclic acid(HL)	$LnL_2(OH)H_2O$ (Ln=La, Pr, Nd, Sm, Gd, Dy, Er, Yb, Y)	33
2-Butyrylcyclo-hexanone(HL)	$LnL_2(OH)H_2O$ (Ln=La, Pr-Gd)	34
2-Hydroxy-1,4-naph-thoquinone(HL)	LnL_3 (Ln=La, Pr, Nd, Sm); $LnL_3 \cdot H_2O$ (Ln=Ce, Gd, Dy)	35
Ethyl acetoacetate(HL)	$LnL_2(OH)H_2O$ (Ln=Y, La, Pr, Nd, Sm, Gd, Dy, Er, Yb)	36
Triethylenetetraamine -N, N, N', N', N'', N''-hexaacetic acid(H_6L)	$LnL_2 \cdot nH_2O$ (Ln=La,Ce,Pr, Nd,Sm,Eu, Gd;n=1,2,3)	37
Salicylhydrazide(HL)	LnL_3 (Ln=La, Pr, Nd, Sm, Er, Y)	38



(III)



(IV)



(V)

1:5 Synthetic Methods for Different Kinds of Lanthanide Complexes[14]

(A) Synthetic Methods for Molecular Complexes of Lanthanides

Molecular complexes of lanthanides are normally prepared by the direct reaction between the salts of lanthanides(LnX_3) and the ligands(L) in a suitable solvent or in the absence of a solvent according to equations [1-5], [1-6], and [1-7].

$$LnX_3 + nL + mSolv. \longrightarrow LnX_3 \cdot nL \qquad [1\text{-}5]$$

$$LnX_3 + nL + mSolv. \longrightarrow LnX_3 \cdot nL \cdot mSolv. \qquad [1\text{-}6]$$

$$LnX_3 + nL \longrightarrow LnX_3 \cdot nL \qquad [1\text{-}7]$$

The ligand exchange method is also important. It is based on the displacement of ligands from molecular adducts of lanthanides of comparatively low stability by another stronger ligand expressed in equation [1-8].

$$LnX_3 \cdot nL + mL' \longrightarrow LnX_3 \cdot mL' + nL \qquad [1\text{-}8]$$

(B) Synthetic Methods for Inner Lanthanides Complexes

There are three main synthetic methods for this type of lanthanide complex ··.

(1) By the direct reaction of derivatives of the lanthanides (salts, alcoholates, etc.) with chelate-forming ligands having acidic EH groups. Although inner complex compounds containing a nitrogen chelation centre are known, the bulk of the inner complex compounds have been prepared using ligands with a hydroxyl group (E=O).

(2) By metal exchange, in which a lanthanide salt is mixed with a chelate compound or salt (mainly of ammonium, alkali metals, or alkaline earths) which contains another metal central atom in solution, and the metal atom in chelate compound or salt is exchanged by the lanthanide ion. This process is described by equation [1-9].

$$3M_nCh + nLn^{3+} \longrightarrow Ln_n(Ch)_3 + 3nM^+ \qquad [1\text{-}9]$$

where Ch denotes a chelate anion, and M=Li, Na, K, or NH_4.

(3) By the chelate exchange method which is based on the displacement of one chelate-forming ligand by another chelating

ligand from the coordination sphere of the inner complex compounds.

$$Ln(Ch)_3 + 3HCh' \longrightarrow Ln(Ch')_3 + 3HCh \qquad [1\text{-}10]$$

(C) Synthetic Methods for Organometallic Complexes of Lanthanides

Synthetic methods of organometallic complexes for lanthanides are similar to the preparation methods of general organometallic compounds.[14] They are described below.

(1) By the direct synthesis from metals in liquid ammonia or in a medium of an unsaturated hydrocarbon,[39] as described in the equation [1-11].

$$6C_5H_6 + 2Ln^0 \longrightarrow 2[(C_5H_5)_3 Ln] + 3H_2 \qquad [1\text{-}11]$$

(2) From the reaction between metallic derivatives of ligands and anhydrous lanthanide halides.

$$3RM + LnX_3 \longrightarrow R_3Ln + 3MX \qquad [1\text{-}12]$$

where R is an organic derivative (e. g., the cyclopentadienyl anion $C_5H_5^-$, Ln is a lanthanide, M = Na, Li; X=halide[40]).

1:6 The Choice of Synthetic Conditions for Lanthanide Complexes[14]

Generally, the most important conditions for the synthesis of lanthanide complexes are the solvent, and the temperature (in aqueous solution, the pH of the medium, is important).

(A) Solvents More and more non-aqueous solvents have been used to prepare various lanthanide complex compounds as the advance of the synthetic chemistry of the lanthanides.

Alcohols are one kind of pure organic solvent which are extensively used. For instance, methanol is a good organic solvent for preparation of lanthanide complexes.[41,42] It has a number of advantages, (a) most of the lanthanide salts and ligands are highly soluble; (b) the solvating ability of methanol for cations is low; and (c) the dielectric constant of methanol is comparatively high; all of these create very favorable conditions. Ethanol is a good organic solvent and is often used as an alternative. Some other solvents have also been extensively used to prepare lanthanide complexes. Examples of these solvents are: benzene,[43-47] acetonitrile,[48-58] acetone,[48,59-61] ether-hydrocarbon mixtures,[50,56,62] triethyl orthoformate.[51,57] The advantages of non-aqueous solvents in the preparation of lanthanide complexes are clear and some of the main points are listed below.

(i) the hydrolyses of lanthanides and their complexes are prevented in non-aqueous solvents, especially when using highly

basic ligands.

(ii) various organic compounds serving as ligands and the organic derivatives of lanthanides employed as sources of the metals are easily dissolved in these solvents so it benefits the expected synthesis.

(iii) by avoiding the use of water, it becomes possible to obtain lanthanide complexes with constant compositions since they do not contain coordinated water molecules.

(B) Temperature Conditions The temperature conditions for the preparation of the lanthanide complexes have not yet been a subject of any systematic study, but according to general arguments it is possible that an endothermic reaction would benefit from an increase in temperature and an exothermic reaction would benefit from a decrease in temperature. Most of the direct reactions of lanthanide salts with ligands are exothermic reactions,[14] so the temperature for the preparation of lanthanide complexes requires rigid control. Normally, the effects observed from an increase in temperature during the preparation of the complexes are:

a) thermolysis of the complexes;

b) the production of complex compounds with undesirable qualitative and quantitative compositions;

c) the occurrence of secondary processes, especially the precipitation of lanthanide hydroxides from the reaction

mixture.

1:7 Bonding Characteristics and Absorption Spectra of the Lanthanide Complexes

Moeller et.al. have made many physical studies of magnetic, spectral and structural data and have concluded that the bonding in the coordination compounds of lanthanide ions may be considered as involving electrostatic interactions.[13]

The absorption spectra of lanthanide ions and their complexes have been investigated in detail.[63-69] The intensities and positions of the absorption bands have been studied and found to be a function of the nature of the lanthanide, the ligand environment, and the solvent. In the far ultraviolet, the ions of some lanthanides have absorption bands corresponding to the allowed 4f-5d transitions;[70] in the visible region, absorption bands associated with the 4f-4f transitions of the electrons are observed.[71] In conformity with theory[64,71], the strengths of the 4f-4f absorption bands are rather small. When the environment of the lanthanide(III) ions is altered, appreciable strengths are observed only for certain absorption bands corresponding to the 4f-4f transitions. This kind of 4f-4f transition is referred to as a hypersensitive transition(HST). The mechanism of these hypersensitive transitions has been explained[63,72] in terms of the weakly covalent nature of the Ln^{3+}–ligand bond.

1:8 Solvation of Some Ln(III) Cations in Acetonitrile

J.-C. G. Bunzli et.al, studied the solvation of Eu(III) and Tb(III) ions in anhydrous acetonitrile by means of conductimetry, vibrational spectroscopy, and fluorescence measurements.[73] The result of conductimetric measurements on the solution of europium nitrate in strictly anhydrous acetonitrile indicated that essentially no dissociation occurred. The vibrational spectra showed the presence of coordinated acetonitrile and coordinated nitrate. They found that a maximum of four acetonitrile molecules were directly bound to the Eu(III) ion, with three bidentate nitrate groups coordinated, so the Eu(III) ion was ten-coordinate. When the total concentration of nitrate in solution was increased, the coordinated acetonitrile molecules were gradually displaced by nitrate groups until the pentanitrato species $[Eu(NO_3)_5]^{2-}$ was formed. There is a strong interaction between the nitrate groups and the Eu(III) ion. A weak fluorescence band around 580 nm was assigned to the transition $^5D_0 \dashrightarrow {}^7F_0$ of the Eu(III) ion. In the case of the Tb(III) nitrate, the result of conductimetric measurements on strictly anhydrous acetonitrile solution led to the same conclusion as found for Eu(III). It was found that three acetonitrile molecules belong to the first solvation sphere but the experimental facts pointed to a smaller coordination number possibly nine for Tb(III) compared to Eu(III). J.-C. G. Bunzli et.al., also studied the solvent effects of acetonitrile on the absorption spectrum of $Nd(ClO_4)_3$ in solution.[74] They found the four more intense absorption bands in the visible region of Nd(III) spectrum which were assigned to be transitions:

$^4I_{9/2}$ ------> $^2H_{9/2}$, $^4F_{5/2}$ (~800 nm);

$^4I_{9/2}$ ------> $^4S_{3/2}$, $^4F_{7/2}$ (~750 nm);

$^4I_{9/2}$ ------> $^4G_{5/2}$, $^2G_{7/2}$ (~580 nm);

$^4I_{9/2}$ ------> $^4G_{9/2}$, $^4G_{7/2}$, $^2K_{13/2}$ (~520 nm).

The coordination number of the Nd(III) was regarded as nine, the same as it is in aqueous solution.

1:9 Electronic Spectra of Some Lanthanide(III) Ions in Anhydrous Hydrogen Fluoride

Electronic spectra of the cations praseodymium(III) and neodymium(III) in anhydrous hydrogen fluoride(AHF) have been investigated by C. G. Barraclough, R. W. Cockman and T. A. O'Donnell.[75] The fluorides of these cations are not sufficiently soluble for spectra to be observed by conventional procedures. So they treated the suspensions of the fluorides with boron trifluoride to prepare solutions of sufficient concentration. They found that the spectra of these ions are similar in both anhydrous hydrogen fluoride and water. Four bands were observed for Pr(III) in both AHF and H_2O. They were attributed to the transitions:

$^3H_4$ —> $^3P_2$ (440 nm in AHF, 445 nm in H_2O);

$^3H_4$ —> $^3P_1$, $^1I_6$ (465 nm in AHF, 469 nm in H_2O);

$^3H_4$ —> $^3P_0$ (477 nm in AHF, 482 nm in H_2O);

$^3H_4$ —> $^1D_2$ (586 nm in AHF, 589 nm in H_2O).

Eight bands were observed for Nd(III) ion in both AHF and H_2O. They were assigned to the transitions:

$^4I_{9/2}$ --> $^4D_{3/2}$, $^2I_{11/2}$, $^4D_{5/2}$, $^4D_{1/2}$, $^2I_{15/2}$,
(344, 351 nm in AHF, 345, 354 nm in H_2O);
$^4I_{9/2}$ --> $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$,
(507, 519 nm in AHF, 512, 522 nm in H_2O);
$^4I_{9/2}$ --> $^2G_{7/2}$, $^4G_{5/2}$, (572 nm in AHF, 575 nm in H_2O);
$^4I_{9/2}$ --> $^4F_{7/2}$, $^4S_{3/2}$ (735 nm in AHF, 740 nm in H_2O);
$^4I_{9/2}$ --> $^4F_{5/2}$, $^2H_{9/2}$ (791 nm in AHF, 794 nm in H_2O);
$^4I_{9/2}$ --> $^4F_{3/2}$ (861 nm in AHF, 865 nm in H_2O);

The intensities of these bands were lower in anhydrous hydrogen fluoride and there were small frequency shifts to a higher energy. However, although the absolute intensities in anhydrous hydrogen fluoride were lower, the relative intensities of these bands in both anhydrous HF and water were remarkably similar. with one exception, the shoulder appearing at approx. 800 nm in water for Nd^{3+} was weaker than that in anhydrous hydrogen fluoride. The close similarity between the relative intensities of their absorption spectra in both H_2O and AHF supported the idea of the coordination numbers of Pr(III) and Nd(III) in AHF being both nine, the same as that in water.

1:10 Aim of the Present Work

In the previously reported work, the behaviour of UF_6, MoF_6, and WF_6,[76,77] as well as some NO^+ compounds[78] towards

transition metals and post-transition metals in acetonitrile has been extensively studied. The behaviour of these hexafluorides and the NO^+ compounds towards the lanthanide metals has, however, not been reported, although the oxidation of europium metal by $NO^+BF_4^-$ in acetonitrile is known.[79] The aim of the work described in this thesis, was to study the reactions between these hexafluorides and some lanthanide metals in acetonitrile, and thus give an insight into the systems. Hence to determine their synthetic utility with particular reference to ligand displacement reactions in which coordinated acetonitrile would be displaced by other simple ligands. This type of reaction is difficult to perform in water since the latter is a good ligand towards Ln^{3+} cations.

The lanthanide metals used in the present study are lanthanum, neodymium, europium, and thulium. The first three belong to the "light group" and the last one belongs to the "heavy group".

The ligands used in this work are the simple N–donor species, trimethylamine(NMe_3) and pyridine(py). They are regarded as comparatively weak ligands compared with chelating and macrocyclic ligand which possess greater stabilizing ability. The main objective of selecting NMe_3 and py as ligands in the present work was to determine whether they can displace acetonitrile from solvated lanthanide cations in acetonitrile. The ligands are volatile and, the hexafluorides used, as well as the compounds prepared are sensitive to moisture, therefore, it was necessary to use a high vacuum technique.

1:11 Acetonitrile–an Ideal Solvent for Non-aqueous Chemistry of Cations

Protonic and aprotic solvents are both used to study the non-aqueous chemistry of cations. Protonic solvents, for example, liquid ammonia, are self-ionizing with the ionization taking place through the transfer of a proton from one solvent molecule to another. The result of this transfer of a proton is the formation of a solvated proton, and a deprotonated anion. The so-called aprotic solvents are those which do not involve the transfer of a proton. According to their natures, the aprotic solvents are divided into three groups.[80] The first group is called non-polar and does not undergo self-ionization so that it behaves as a non-solvating property. Benzene and cyclohexane are examples of this kind of solvent. The second group consists of those solvents which are polar but do not ionize to an appreciable extent, such as acetonitrile and dimethylsulphoxide(DMSO). Solvents of this group are of a good coordinating ability owing to their polarity which ranges from low (SO_2) to extremely high (DMSO). Most solvents of this group are Lewis bases. Solvents which are both highly polar and self-ionizing form the last group, one example of this group is bromine trifluoride.

Acetonitrile is an aprotic dipolar solvent with a relatively high dielectric constant, 37.5 at 25°C,[81] so it is a suitable solvent for many ionic compounds. Its volatility, m.p.=-45.7; b.p.=81.6°C, makes it ideal for vacuum line work at ambient temperatures, and it can be easily handled in greaseless, Pyrex apparatus.

Acetonitrile has a large working potential range of 5.7v. It is a strong enough Lewis base to solvate effectively a large number of high oxidation state, covalent fluorides and metal cations, particularly those of 3d and post-transition elements, and it can be easily displaced by some other stronger bases, for example F^- ion. Acetonitrile has a simple vibrational spectrum and is transparent in the visible and u.v. regions. These properties, as well as the availability of CD_3CN, make it an ideal solvent for spectroscopic work.

The coordination nature of acetonitrile to a metal cation, as well as the role of acetonitrile as a donor solvent has been extensively reviewed.[82] In most cases the coordination process involves acetonitrile binding to a metal ion through the lone pair of electrons on nitrogen. This results in an increase in the vibrational stretching frequencies of the C≡N and C-C in comparison with those of the free acetonitrile molecules.[83] This is mainly attributed to the enhancement of the C≡N stretching force constant of the sigma bond system that results from a shortening of the C≡N bond.[84] The increase in the infrared stretching frequency of the C≡N bond is important evidence in identifying the presence of coordinated acetonitrile.

Commercial acetonitrile usually contains some impurities which would affect the results of expected reactions, so it must be carefully purified before use. The detailed description of the purification method for acetonitrile is given in chapter two.

1:12 Lewis Acid–Lewis Base Reactions

Work previously carried out in acetonitrile showed that ionic metal chlorides(as Lewis bases) react with covalent chlorides(as Lewis acids) in acetonitrile.[85] Some of complexes with the formula, $[M(MeCN)_n][SbCl_6]_2$ (M=Fe, Co, Mn, Ni, Cu, Zn and n=4 or 6) have been prepared by the reaction between $SbCl_5$ and metal chlorides in acetonitrile.[86] Also the salts with the formula $[MCl_x(MeCN)_{6-x}][SbCl_6]$, have been obtained by the reaction of transition metal halides(as the Lewis bases), MCl_n (M=Ti, n=4; M=V, n=3; M=Fe, n=2,3) with $SbCl_5$(as the Lewis acid) in acetonitrile.[87]

Heterogeneous Lewis acid-base reactions involving metal binary fluorides as Lewis bases and covalent high oxidation state fluorides as Lewis acids, have been used to obtain solvated metal cations in acetonitrile. For instance, Cu(II) and Tl(I) heptafluorotungstates(VI) have been prepared by the reaction between CuF_2 or TlF and WF_6 in acetonitrile.[88] Similarly, TaF_5, AsF_5 and PF_5 react with CuF_2 to generate the corresponding solvated Cu(II) hexafluoroanion salts.[89]

The complex fluoro-anions generated in the above reactions, generally showed little tendency to coordinate with the metal ion, as compared with the greater coordinating ability of chloroanions. This is perhaps because of lower electronegativity of chlorine, thus making it easier to form chlorine bridges. This property of minimal coordination ability of fluoro-anions is very

important because only the solvent is in the first coordination sphere of the complex cation and so the study of metal cations becomes simple to some extent.

1:13 Some Properties and Reactions of the Hexafluorides UF_6, MoF_6 and WF_6

The oxidation of metals and non-metals by covalent high oxidation state fluorides has been extensively studied. The relative oxidizing abilities of the 4d and 5d transition metal fluorides have been well-investigated.[76,77,90] Some fluorides have a very strong oxidizing ability and will interact with the acetonitrile, causing it to polymerise, and therefore are not suitable for use. However, the hexafluorides of uranium, molybdenum and tungsten are several examples which are commonly studied and used. In general the hexafluorides studied possess orthorhombic symmetry in their solid lattices. The hexafluorides of uranium, molybdenum and tungsten are monomeric and octahedral, that is, the metal atoms occupy octahedral holes, and six fluorine atoms surround the central metal atoms. Detailed studies have been made of MoF_6 and WF_6 by neutron powder diffraction,[91] and comparison of results with similar work on UF_6 indicates that MoF_6 and WF_6 are more compact and spherically shaped molecules than UF_6 in the solid state. The bond-stretching force constants of the fluorine to metal bond for the hexafluorides of uranium, molybdenum and tungsten have been calculated from spectral data, the values are 5.13 md/Å for WF_6, 4.73 md/Å for MoF_6 and 3.78 md/Å for UF_6.[92] These values indicate that the order of bonding strength

is $WF_6 > MoF_6 > UF_6$.

The electron affinities of the hexafluorides of uranium, molybdenum and tungsten have been determined by various methods, for instance, ion cyclotron resonance spectroscopy,[93,94] molecular beam reactions with alkali metals,[95,96] hexafluoride oxidation of graphite,[97,98] thermochemistry of hexafluorometallate(V) salts,[99,100] and effusion mass spectroscopy.[101,102] Although different values were obtained for each method used, all results show the same trend in electron affinities, i.e. $WF_6 < MoF_6 < UF_6$.

Electron affinities of the hexafluorides have also been estimated from the electronic spectra of the charge transfer complexes of the hexafluorides.[103-105] The order found is consistent with their gas phase redox chemistry.[106,107] The oxidizing abilities of the hexafluorides of uranium, molybdenum and tungsten have been demonstrated by a number of redox reactions both in the gas phase and the solution state. O'Donnell and Stewart investigated[107] the reaction between uranium, molybdenum and tungsten hexafluorides and some lower fluorides of non-metals, for example, phosphorus , arsenic, antimony and bismuth trifluorides. Uranium hexafluoride reacts readily with PF_3, whereas the reduction of MoF_6 was only partial. This is because the phosphorous pentafluoride formed is capable of oxidizing molybdenum pentafluoride. Reduction of tungsten hexafluoride by PF_3 was very slow and occurred only to a limited extent. Addition of anhydrous hydrogen fluoride

appears to be necessary to catalyse the reaction. Nitric oxide is found to react with UF_6 and MoF_6, when the two gases are condensed into an evacuated nickel reactor[106] or in a Kel-F tube[108] and the reaction mixture is allowed to warm up to room temperature, salts of the general formula, $NO^+MF_6^-$, are formed, thus the central atom of a hexafluoride is reduced to a pentavalent state. However, tungsten hexafluoride does not react with nitric oxide even at 100°C. All these gas phase reactions indicated that uranium hexafluoride and molybdenum hexafluoride have comparable oxidizing ability whereas tungsten hexafluoride is found to be the weakest among the three oxidizing agents.

The reactivity of the hexafluorides of uranium, molybdenum and tungsten in solution has been studied in a number of ways. The redox couples MF_6/MF_6^-(M=Mo, W) have been identified in anhydrous hydrogen fluoride, Bond et. al.[109(a)] using the technique of cyclic voltammetry at platinum and glassy carbon electrodes. The redox process is a simple one-electron transfer reaction.

$$MF_6 \underset{e^-}{\overset{e^-}{\rightleftharpoons}} MF_6^- \quad M=Mo,\ W. \qquad [1\text{-}13]$$

The electrochemical potential values of the couples MF_6/MF_6^- are determined by measuring the half wave potentials given, $E_{1/2}(MoF_6/MoF_6)$=+0.91v and $E_{1/2}(WF_6/WF_6^-)$=-0.11v versus CuF_2/Cu. A comparision of the two couples shows WF_6 to be a

mild oxidizing agent and molybdenum hexafluoride is a stronger oxidizing agent. No electrochemical data of uranium hexafluoride in anhydrous hydrogen fluoride are available. Uranium can be reduced by hydrazinium(+2) at $0^{o}C$ in hydrogen fluoride or carbon tetrachloride. If excess of uranium hexafluoride is used, the product of the reaction is hydrazinium(+2)hexafluorouranate $[N_2H_6(UF_6)_2]$. With excess hydrazinium(+2) fluoride, the product is hydrazinium(+2)heptafluorouranate(V) $[N_2H_5UF_7]$.[109(b)]

Molybdenum hexafluoride and tungsten hexafluoride react with alkali metal iodides in sulphur dioxide medium. Both hexafluorides are reduced to their respective hexafluorometallates(V),[110] according to the equations:

$$2MoF_6 + 2MI \xrightarrow{SO_2} I_2 + 2MMoF_6 \qquad [1\text{-}14]$$

$$2WF_6 + 2MI \xrightarrow{SO_2} I_2 + 2MWF_6 \qquad [1\text{-}15]$$

(M=alkali metal, except Li)

The oxidizing abilities of the hexafluorides of uranium, molybdenum and tungsten towards iodine in iodine pentafluoride have been investigated. The work was performed in this department by Berry et.al.[110] Molybdenum and tungsten hexafluorides were both inert towards iodine in iodine pentafluoride medium. However, uranium hexafluoride oxidized I_2 to I_2^+ in IF_5. The behaviour of uranium hexafluoride towards

iodine in iodine pentafluoride depends on the stoichiometry of the reaction. If the mole ratio of UF_6 to I_2 is 1:1, the I_2^+ formed immediately, but when the mole ratio of UF_6 to I_2 is 10:1, the product, $I_2^+UF_6^-$, undergoes a complete decomposition to UF_5 and IF_5, as presented by the equation below:

$$10UF_6 + I_2 \longrightarrow 10UF_5 + 2IF_5 \qquad [1\text{-}16]$$

This behaviour of the hexafluorides of tungsten, molybdenum and uranium towards I_2 in IF_5, is consistent with similar work involving the reaction of I_2 with the hexafluorides at high temperature.[111] Molybdenum and tungsten hexafluorides do not react with iodine whereas uranium hexafluoride undergoes the reaction.

$$3I_2 + 20UF_6 \longrightarrow 6IF_5 + 10U_2F_9 \qquad [1\text{-}17]$$

The non-volatile uranium fluoride, U_2F_9, presumably arises from the disproportionation of UF_5.

Molybdenum, tungsten and uranium hexafluorides, in acetonitrile are capable of oxidizing a number of transition metals and post-transition metals to give solvated metal cation salts of the appropriate MF_6^- anion.[76,77] Molybdenum hexafluoride and uranium hexafluoride show an appreciable similarity in their behaviour towards some transition metals. Previously reported work showed that copper and cadmium react with the molybdenum and uranium hexafluorides, in acetonitrile, forming the products, $[A(MeCN)_5(MF_6)_2]$, (A=Cu and

Cd; M=Mo and U). Tungsten hexafluoride oxidized Cu to Cu^{I} in acetonitrile. Tungsten hexafluoride reacted differently, probably because of the similarity in the potential values of the couples Cu^{II}/Cu^{I} and WF_6/WF_6^-, and also because of a fluoride ion transfer reaction.[76]

$$WF_6^- + WF_6 = WF_7^- + WF_5 \qquad [1\text{-}18]$$

Cyclic voltammetry has been used to identify the redox couples MF_6/MF_6^- in acetonitrile (M= U, Mo and W). The half wave potentials are, respectively, $E_{1/2}(UF_6/UF_6^-)=+2.33v$, $E_{1/2}(MoF_6/MoF_6^-)=+1.60v$, and $E_{1/2}(WF_6/WF_6^-)=+0.51v$ versus Ag^+/Ag. The differences between $E_{1/2}(MoF_6/MoF_6^-)$ and $E_{1/2}(WF_6/WF_6^-)$ in HF and MeCN, are almost identical. The order of oxidizing ability, in acetonitrile, determined from combination of cyclic voltammetry and redox chemistry is shown to be $UF_6 > MoF_6 > WF_6$.[77]

Molecular iodine is oxidized by UF_6 and MoF_6 but not by WF_6, in acetonitrile, to give isolable salts $[I(MeCN)_2(MF_6)]$, (M= Mo or U).[112] This behaviour is in contrast to that observed in IF_5 solution[110] where iodine I_2 is oxidized to I_2^+ by UF_6 but not by MoF_6 and WF_6. Cobalt can be oxidized in acetonitrile to give solvated salts $[Co(MeCN)_6(MF_6)_2]$ (M=Mo, or W) by MoF_6 and WF_6. Neither MoF_6 nor UF_6 is able to oxidize massive nickel. Molybdenum hexafluoride, however, can oxidize chemically cleaned nickel metal or vacuum evaporated nickel film and tungsten hexafluoride reacts easily with massive nickel.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

A number of techniques were used to carry out the reactions and to identify the solid complex compounds. It was necessary to take special care to exclude even traces of water, because most of the compounds and reagents were sensitive to moisture. The techniques and procedures used are described in this chapter.

2:1 Vacuum Line and Glove Box Techniques

As anhydrous reagents were used and the compounds prepared were sensitive to moisture, vacuum line and glove box techniques were very important. All manipulations were performed under vacuum or in an inert dry atmosphere box. A conventional high vacuum Pyrex system met the necessary requirement. The Pumping system consisted of an "Edwards high vacuum" rotary oil pump and Jencons glass mercury diffusion pump arranged in series to give a vacuum better than 0.001 Torr. Standard glass joints were greased with Apiezon black wax, Voltalef Kel-F or high vacuum Apiezon N. grease as appropriate. All reactions were performed in Pyrex double limb reaction vessels (Fig. 2.1) which were carefully flamed out and evacuated to remove adsorbed moisture before use. Some of the high oxidation state fluorides used as oxidizing agents were stored over activated sodium fluoride, NaF, (acting as a trap for trace hydrogen fluoride) in breakseal ampoules (Fig. 2.2) which were joined to the vacuum line by a gas/oxygen torch. This arrangement avoided the use of a stop-cock, the vessel being opened by dropping a glass-sheathed iron bar onto the seal by means of a magnet.

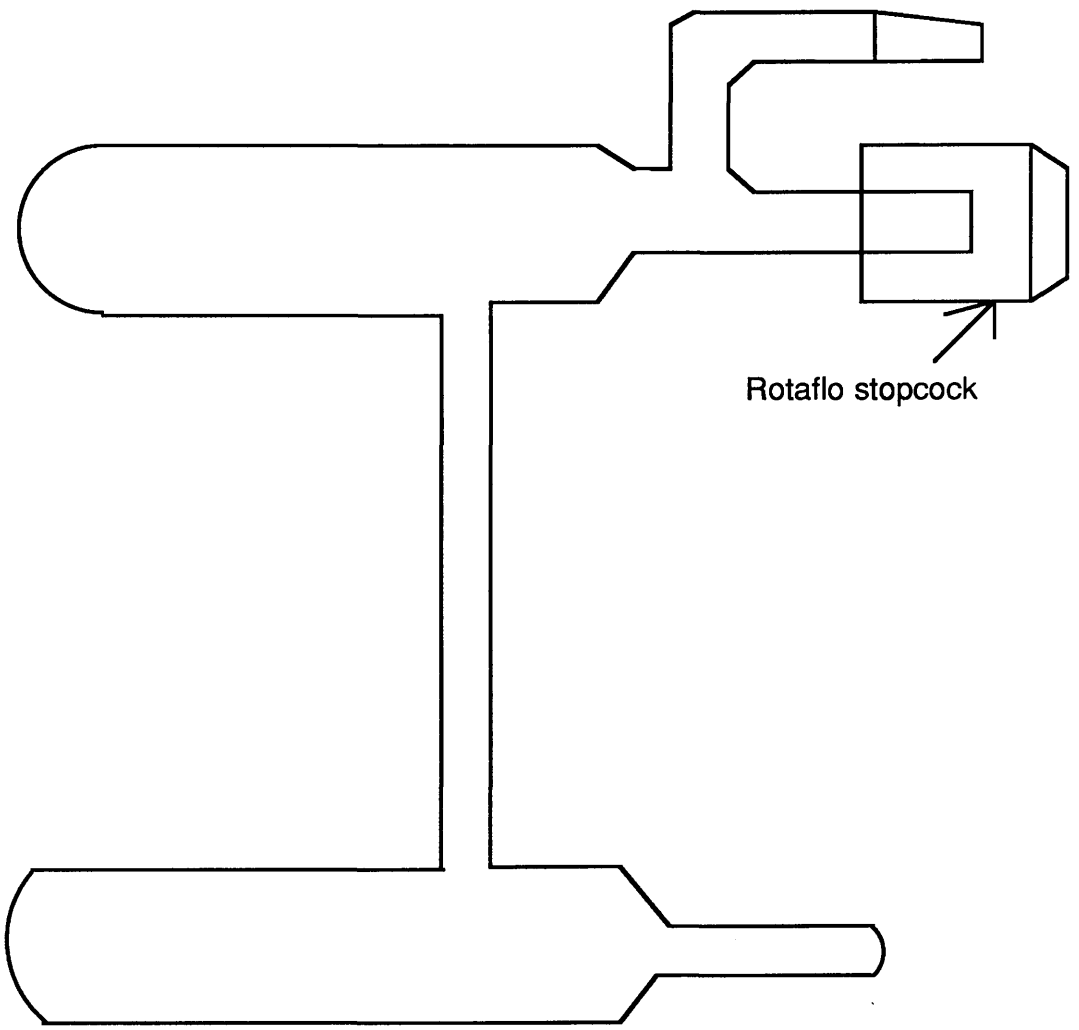


Fig. 2.1 Double-limb reaction vessel

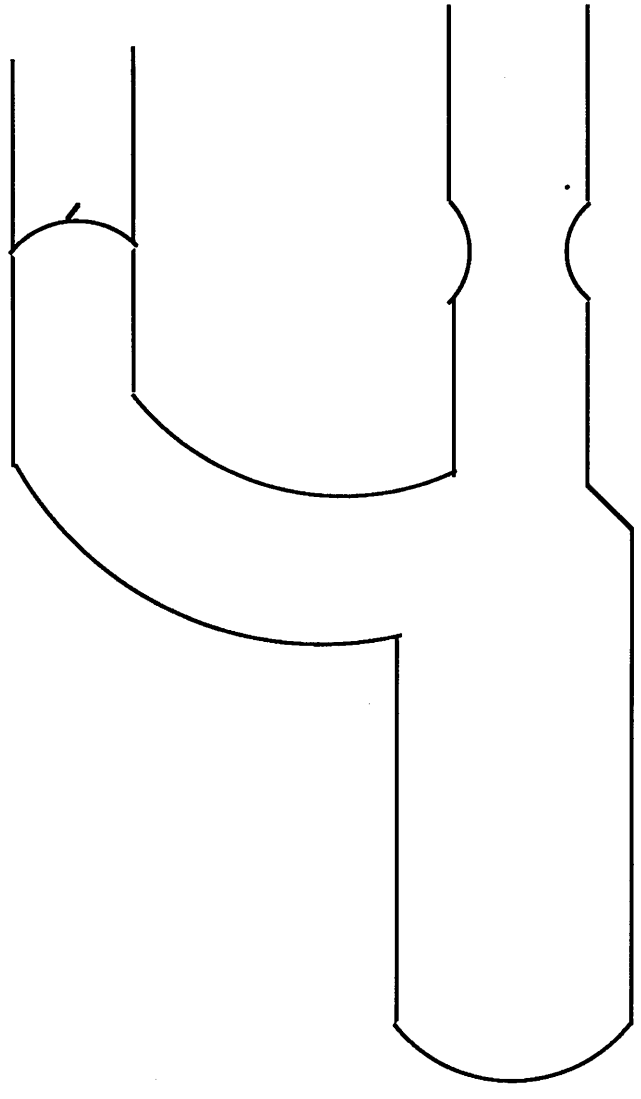


Fig. 2.2 Breakseal vessel

The loading and unloading of hygroscopic chemicals and involatile materials, and the preparation of analytical samples were carried out in a nitrogen atmosphere glove box (Lintott Engineering Co. Ltd.) in which the concentration of water was kept below 10 p.p.m.. The glove box had an evacuable air-lock so that apparatus and materials could be introduced into the glove box without disturbing the dry conditions inside. The moisture and oxygen were removed by recirculation over molecular sieves and manganese oxide respectively.

2:2 Vibrational Spectroscopy [114,115,116]

Infrared and Raman spectroscopy are very important methods used to identify unknown compounds. They are widely used to investigate a variety of molecules in the solid, liquid and gas states. Infrared and Raman spectroscopy are based on different interaction mechanisms between radiation and the molecules, so the quantum mechanical selection rules are also different. Therefore, not all of the molecular motions recorded by one type will necessarily be recorded by the other. However, both methods can supply complementary information about molecular structure. Vibrational spectroscopy was used to identify the organic ligands and inorganic anions in the compounds synthesized.

A molecule will absorb infrared radiation if it vibrates in such a way that its electric dipole moment changes during a normal mode of vibration, whereas observation of Raman scattering depends on a change in the polarizability of a bond during the

vibration. According to the mutual exclusion rule, in a polyatomic molecule with a centre of symmetry, the vibrations anti-symmetric with respect to the centre of symmetry are infrared active and forbidden in the Raman, but the vibrations symmetric with respect to the centre of symmetry are Raman active and forbidden in the infrared.

The information obtained from vibrational spectroscopy is directly related to the symmetry of a molecule. A vibrational frequency depends on a force constant which is in turn related to the bond strength. When a free ligand is coordinated to an atom or ion, some of these criteria change and these kinds of changes also affect the spectra, resulting in changes in band intensities and positions. Naturally the force constant would change, so the vibrational spectra of coordinated ligands differ appreciably from those of free ligands, and it is expected that a change in the spectrum results from a change in geometry of a molecule. In the present work, for example, because of coordination of acetonitrile via nitrogen, the force constant of the C≡N bond is greatly increased due to a strengthening of the σ binding between C and N. In addition to its "s" character, the N lone-pair orbital will aquire an amount of "p" character upon coordination. This means an increasing amount of "s" character in the C≡N bond, resulting in an increasing force constant, so that the stretching frequency of the C≡N is shifted to higher wave number.[83,117]

According to Group Theory, one can predict the number of the

bands expected in the spectrum of a molecule from the symmetry of the molecule. For instance, the acetonitrile molecule belongs to the point group C_{3v}, and has eighteen degrees of internal freedom. The eighteen Cartesian displacement vectors for the entire molecule generate the reducible representation Γ given below:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	18	0	4

The representation Γ can be reduced to:

$$\Gamma = 5A_1 + A_2 + 6E$$

The C_{3v} character table shows that A_1+E are translations and A_2+E are rotations, then, the internal vibration are $4A_1+4E$. Inspection of the group C_{3v} character table indicates that the A_1 and E modes of vibration are both infrared and Raman active.

In the case of the octahedral complex fluoroanions, MF_6^- (M=P, Mo, W,or U), the point group is O_h and, the twenty one Cartesian displacement vectors from a basis for the representation:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_s$	$6\sigma_d$
Γ	21	0	-1	3	-3	-3	-1	0	5	3

The representation Γ reduces to:

$$\Gamma = A_{1g} + Eg + T_{1g} + 3T_{1u} + T_{2g} + T_{2u}$$

From the O_h character table, it is apparent that the translations account for T_{1u} and the rotations for T_{1g}, leaving as internal vibrations:

Infrared active:	$2T_{1u}$
Raman active:	A_{1g}, E_g, T_{2g}
Inactive:	T_{2u}

2:2a Sample Preparation for Infrared Spectroscopy

For solid samples, a small amount (2-5 mg) of the solid was finely ground using an agate pestle and mortar, then a mull or paste was made by adding a drop of liquid paraffin oil, Nujol, or a fluorinated liquid polymer, Fluorolube. A little paste was placed between two AgCl or Si plates which were mounted in a suitable sample holder (Fig. 2.3). Nujol is a suitable mulling agent for infrared spectroscopy because it absorbs only at 2900, 1460, 1380, and 725 cm^{-1}. Fluorolube was used to examine those regions where Nujol absorbs. In the case of gases, samples were studied by permitting the gaseous samples to expand into an evacuated 5 cm path length cell at a measured pressure. The cell was made of Pyrex glass with AgCl windows joined to glass with silicon sealant (RS Components Ltd.). An infrared spectrum was recorded over the region 4000-400 cm^{-1} (AgCl plates) or 400-

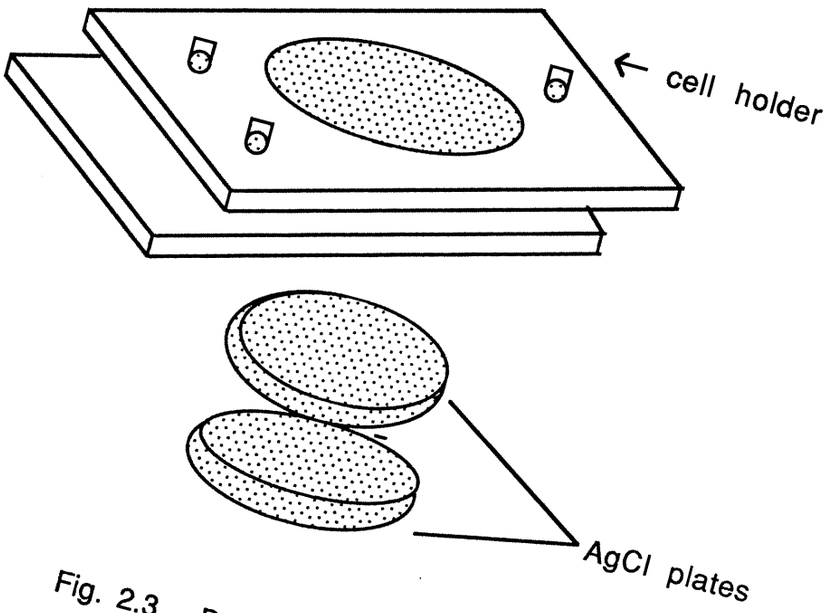


Fig. 2.3 Demountable cell holder

200 cm^{-1} (silicon plates) on a Perkin-Elmer 983 spectrometer with data station.

2:2b Sample Preparation for Raman Spectroscopy

Sample preparation for Raman spectroscopy is very easy, no special plates or cells are required. The solid samples were simply transferred to a Pyrex glass capillary (Fig. 2.4) which was then evacuated and sealed.

2:3 Electronic Absorption Spectroscopy[118,119]

Electronic absorption spectroscopy is also one of the principal methods used in studying the physical and chemical properties of complex compounds. It is associated with electronic transitions in a molecule, or a transition metal ion. These transitions result from the excitation of an electron in the ground state orbital to an orbital of higher energy (the excited state). Electronic transitions which are mainly studied are in the 50,000 to 10,000 cm^{-1} region, that is in the visible and ultra-violet regions of the spectrum, where transitions involving non-bonding and π electrons are involved. Transitions may occur through electric dipole, magnetic dipole or electric quadrupole mechanisms.[120] Different kinds of spectra are described below.

2:3a Charge-Transfer Spectra

Charge-transfer spectra involve the transfer of an electron

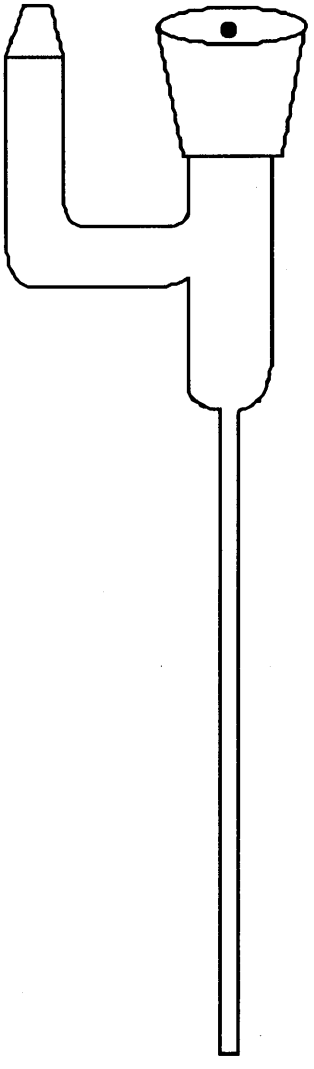


Fig. 2.4 Raman capillary

from an orbital centred mainly on the ligand to one centred mainly on the metal atom (L->M charge transfer) or vice versa (M->L charge transfer). Charge transfer processes are commonly of higher energy than ligand field transitions and usually lie in the ultra-violet or far ultra-violet region. If the metal is easily oxidizable and the ligand readily reducible, or vice versa, then a charge-transfer transition may occur in the visible region. Since the charge-transfer spectra are both spin and Laporte allowed, the spectra are normally very intense and may mask the weaker ligand field transitions if both transitions are close to each other.

2:3b Ligand Spectra

Most organic ligands absorb light in the ultra-violet region. The several kinds of transitions which are possible are:

(1) n-> σ^* Transitions

They correspond to transitions of the internal non-bonding lone pairs to σ^* orbitals, so that they are high energy transitions and generally appear at the shorter ultra-violet wavelengths, for example, acetone absorbs at 190 nm.

(2) π -> π^* Transitions

These transitions correspond to those of the π-bonding orbital in the highest occupied molecular orbital (HOMO) to the π^* orbital in the lowest unoccupied molecular orbital (LUMO). The

π–>π* transitions are usually the least energetic, which results in their appearance at longer wavelengths.

(3) n-> π* Transitions

These transitions are due to transitions of an electron from the non-bonding orbitals of lower energies to π-anti-bonding orbitals of higher energies. This kind of transition occurs in the molecules which have both π-bonding and non-bonding electron pairs, e.g. aldehydes and ketones.

2:3c Ligand Field Spectra

This type of transition is due to the coordination of ligands to the metal ion, which produces a ligand field and results in the splitting of the d-orbitals of a transition metal. Transitions from one energy level to a higher energy level arise from the absorption of radiation; the stronger the ligand field strength, the shorter is the wavelength of bands appearing at the spectrum. Not all transitions possible between different energy levels may be observed. The transitions which can be observed must meet the requirements of the selection rules. Selection rules determine the nature of the transitions and whether a transition is permitted or not. There are two main types as described below.

(1) Spin Forbidden or Multiplicity Forbidden

The transition which does not meet the requirement of

keeping the number of unpaired electrons constant is forbidden, that is, an allowed transition is one in which the spin state of the complex does not change ($\Delta S=0$).

(2) Laporte Forbidden

Transitions involving redistribution of electrons within a single quantum shell are Laporte forbidden. According to the Laporte selection rule, the allowed transitions are s->p, p->d and so on, but d->d and f->f transitions are forbidden. The Laporte forbidden d->d transitions is relaxed to some extent in molecules which do not have a centre of symmetry as mixing of d- and p-orbitals can take place in such molecules. Thus the transitions can occur between d-orbitals containing different amounts of p character. If the metal-ligand bonding in the complex is largely covalent, then the transitions will not be pure d->d transitions as the p-orbitals of the ligand and the d-orbitals of the metal may mix. Even though a molecule is centrosymmetric, if the centre of symmetry can be removed temporarily by an odd vibration, the d->d transitions may occur to a rather small extent.

2:3d Forbidden f->f Transitions[7,26]

A lanthanide ion absorbs light quanta of energy suitable for inducing excitation from its ground state to give its characteristic absorption bands. These transitions can be observed as fairly sharp, weak bands. These very weak bands arise from the fact

that these are f->f transitions which are Laporte forbidden, and the f electrons are very effectively shielded by the overlying $5s^2$ and $5p^6$ shells so that they are only slightly affected by the ligands. Thus the effects such as take place in the ion $[CoCl_4]^{2-}$ where the tetrahedral ligand field introduces some p character into the transition, giving fairly intense absorptions, do not occur in the case of the lanthanides. Generally, there are two characteristic features of the f->f transitions of the lanthanides. One is that the spectra in the visible and near ultra-violet (sometimes in the near infrared) consist of fine lines, almost atomic-like in their sharpness. The other is that the spectra are very weak.

2:3e Sample Preparation

Sample solutions for electronic spectroscopy were kept in the special vessels to protect moisture-sensitive samples, The vessels used had a one-limb reaction vessel provided with a 10 mm Spectrosil cell (Fig. 2.5). Because the samples are moisture-sensitive, the reactions were carried out in the reaction vessel, then the resulting solution was decanted into the Spectrosil cell. The reference cell was a simple cell containing the solvent. The spectra were recorded on a Perkin-Elmer Lambda 9UV/VIS/NIR Spectrophotometer.

2:4 Determination of Magnetic Moment[26,121]

In common with many of the transition elements, most

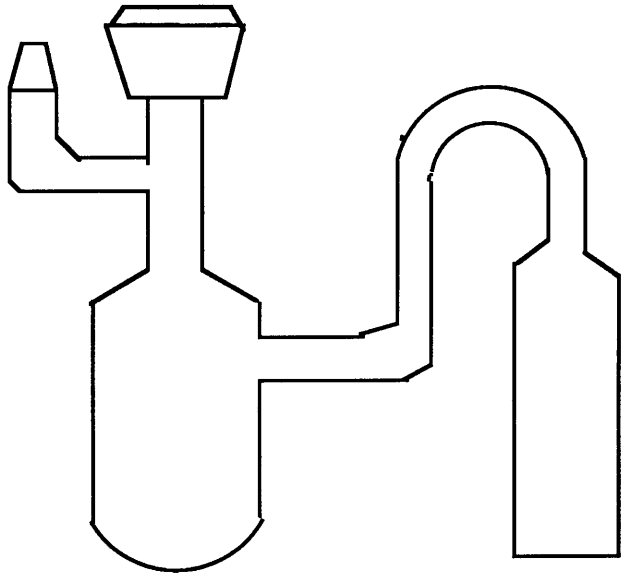


Fig. 2.5 Evacuable cell for electronic spectroscopy

lanthanide cations and their compounds are strongly paramagnetic, that is, they tend to align themselves parallel to a magnetic field. Paramagnetism is associated with the presence of unpaired electrons, which make spin and orbital contributions to the magnetic moment. In the lanthanides, the unpaired electrons lie in the 4f electron shell, that is different from the first and second transition series in which the unpaired electrons are in the 3d or 4d shells. Because 4f electrons are effectively shielded by the overlying 5s and 5p electrons, they do not take part in chemical bonding. Therefore, there is an important difference between the magnetic properties of the lanthanides and the first two series of transition elements. The 3d and 4d electrons can take part in chemical bonding, and as a result their magnetic moments lose the orbital contribution when complexing occurs. In the case of lanthanides, the 4f configurations are virtually unaffected by their environment. This fact is of considerable practical consequence, as it means that the effective moments of free ions, $\mu_{eff}=g_J[J(J+1)]^{1/2}$, where the J is the total angular momentum, are close to the experimental values obtained at high temperature.[122]

The magnetic moments of some lanthanide complexes prepared were determined by the Gouy method which is described below.

Paramagnetic substances are more permeable to a magnetic field than to a vacuum, and the converse is true of diamagnetic substances. These properties are determined by measuring the

force exerted on test samples by magnetic fields of known intensity when a sample, contained in a cylindrical tube, is suspended between the poles of the magnet, the force(F) on the sample in the magnetic field is given by

$$F=g\Delta W=1/2(k-k_{air})H^2A \qquad (2\text{-}1)$$

where g is a constant (981 dyne sec.$^{-2}$), ΔW is a change in weight, k and k_{air} (c.g.s. units) are the volume susceptibilities of the sample and air respectively, H is the magnetic field strength and A the cross sectional area of the sample. H^2A is calculated by measuring a standard substance of known volume susceptibility(k). The volume susceptibility of the specimen can be calculated from knowing H^2A. The gram magnetic susceptibility, χ, of the sample is given by the expression:

$$\chi=k/\rho \qquad (2\text{-}2)$$

where ρ is the density of the sample. The molar susceptibility, χ_m, can be obtained by multiplying the gram susceptibility, χ, with the formula weight of the sample. In order to obtain the virtual magnetic moment of the metal ion alone, a diamagnetic correction should be made using the expression:

$$\chi_m{}^{corr.}=\chi_m\text{-(-diamagnetic correction)} \qquad (2\text{-}3)$$

The effective magnetic moment, μ_{eff}, of the metal ion is given by the equation:

$$\mu_{eff} = 2.84\ (\chi_m^{corr.}\ T)^{1/2} \qquad (2\text{-}4)$$

2:4a Sample Preparation and Experimental Method

A cylindrical glass tube of known volume, fitted with a quickfit stopper, was packed with the sample in the inert atmosphere glove box. The precision and accuracy of the experiment are dependent on the uniformity of the packing and therefore the best procedure was to introduce the powdered sample into the tube a little at a time by means of a micro-spatula. After each addition, the tube was tapped several times on a hard surface. All measurements were made using a Cahn TA 450 micro-balance and a Newport 1 1/2" electromagnet type C. A standard substance, mecury tetrathiocyanatocobaltate(II), $HgCo(NCS)_4$, (χ=16.44×10^{-6} c.g.s. at 293K), was used to calculate H^2A and the value obtained was used to determine the k value of the compound. Another standard substance of known magnetic moment, manganese(III) tris(acetylacetonate), $Mn(acac)_3$, was used to check the correct operation of the equipment. The magnetic moment of $Mn(acac)_3$ was determined to be 4.99 BM (literature value 4.95 BM[123]).

2:5 Preparation and Purification of Some Reagents

2:5a Purification of Acetonitrile[124,125]

Acetonitrile must be carefully purified before use with high oxidation state fluorides. Impurities, particularly acrylonitrile

and benzene, can affect the results of the reactions. For example, some Lewis acid fluorides react with impure acetonitrile to give a brown solid which results from the polymerization of acetonitrile. The purification method used is an extension of the method of Walter and Ramalay[125] and was developed in this department. It consists of a series of steps as follows.

1. Multiple refluxes of HPLC or Spectroscopic grade MeCN supplied in a Pyrex still equipped with a 0.75 m vacuum jacketed separating column, and protected from atmospheric moisture. The solvent was distilled after each reflux and 3% of the initial and final solvent discarded. The sequences of reagents used is shown below, quantities and times are in parentheses.

a. Anhydrous $AlCl_3$ ($15gl^{-1}$, 1h);
b. $KMnO_4$+Li_2CO_3 (both $10gl^{-1}$, 0.25h);
c. $KHSO_4$ ($15gl^{-1}$, 1h);
d. CaH_2 ($20gl^{-1}$, 1h);
e. P_2O_5 ($1gl^{-1}$, 0.5h);
f. as (e).

In the first stage, $AlCl_3$ was used to eliminate acrylonitrile present in the solvent. In the second stage, $KMnO_4$ and Li_2CO_3 were used to eliminate trace amount of aromatic impurities such as benzene and also to neutralize any HCl formed during stage 1. The $KHSO_4$ used in the stage 3 was a strong enough acid to decrease the amine content probably generated from the stage 2. The other stages were used to remove the water present in the solvent so that the acetonitrile was entirely dried.

2. Acetonitrile was transferred without exposure to atmosphere moisture, to a Pyrex glass vessel containing previously activated alumina (neutral, 60 mesh) after step 1. It was then degassed three times in vacuo. The alumina was activated by heating in vacuo at 190 ^{o}C for about 10 hours using an oil-bath.

3. Acetonitrile was then transferred to a Pyrex glass vessel containing previously activated 3A molecular sieves by vacuum distillation, and stored under vacuum until required. The 3A molecular sieves used were activated by heating in vacuo at 190^{0}C for about 24 hours using an oil-bath.

The purified MeCN had an absorbance of 0.05-0.15 at 200 nm and an apparent u.v. cut-off point at ca.175 nm. The U.V. spectrum was recorded using distilled water as a reference.

2:5b Preparation and Purification of WF_6 and MoF_6

Both hexafluorides can be prepared by direct fluorination of the respective metals at high temperature.[126] Tungsten hexafluoride, WF_6, and molybdenum hexafluoride, MoF_6 so prepared can be purified by successive vacuum distillation over activated sodium fluoride, NaF, which absorbs any hydrogen fluoride, HF, generated so that Pyrex glass apparatus can be used to collect the products without corrosion by HF. Since molybdenum hexafluoride (m.p.=17.4^{o}C, b.p.=34^{o}C) and tungsten hexafluoride (m.p.=2.0^{o}C, b.p.=17.1^{o}C) are toxic, highly

hygroscopic substances, they must be handled in a clean, dry, high vacuum system.

The apparatus (Fig. 2.6, 2.7) consisted of a 60 cm long nickel tube equipped with Swagelok couplings, glass apparatus, and a small nickel boat. Pure tungsten, or molybdenum powder (approx. 5g) were loaded into the nickel boat and were spread over the boat as much as possible. The boat was then inserted into the nickel tube and the Swagelok coupling connected. This tube was placed carefully in an oven and one side was attached to a previously prepared Pyrex glass apparatus (Fig. 2.6) using Swagelok couplings with P.T.F.E. ferrules. The Pyrex glass apparatus was immediately linked to a vacuum line and the other side was linked to the fluorine gas cylinder (Fig. 2.8). After the apparatus was evacuated ($\sim 10^{-2}$ torr.), the NaF in traps E. F. G. and I (Fig. 2.8) and the glass section of the apparatus were flamed out with a oxygen/gas torch to activate the NaF and to remove adsorbed moisture. When the apparatus cooled to room temperature, the stopcock, A (Fig. 2.8) was closed and dry nitrogen gas was flushed slowly through the system to bring it to atmospheric pressure. After that, the joint, B, was separated and the nitrogen gas flow (70 cm^3 $min.^{-1}$) continued for about 12 hours.

The oven was switched on and when the reaction temperature of about 320^0C was obtained, the traps C (for trapping moisture from air), G (for collecting products MoF_6 or WF_6), and I (for trapping trace HF) were cooled to -80^0C with

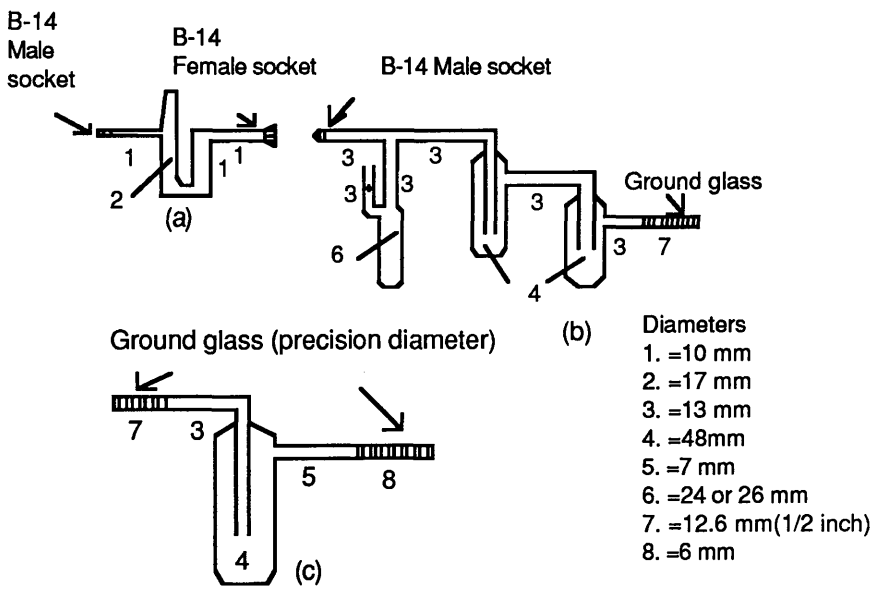
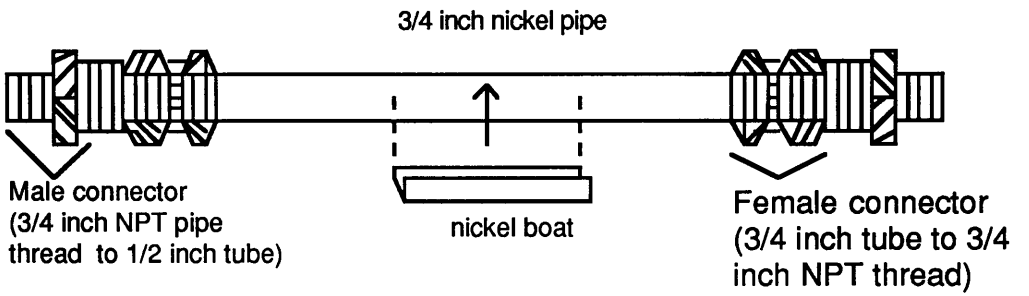


Fig. 2.6 Glass apparatus



* Both connectors are stainless steel(316)

Fig. 2.7 Nickel tube boat

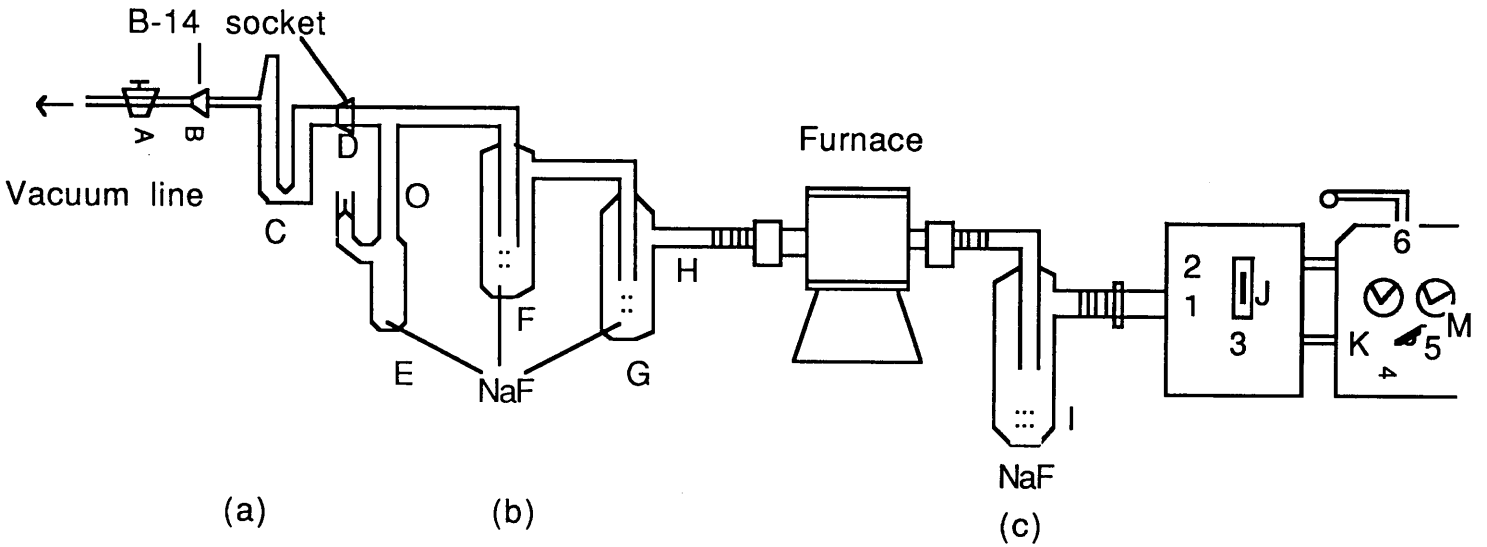


Fig. 2.8 Fluorination system for MoF_6 and WF_6

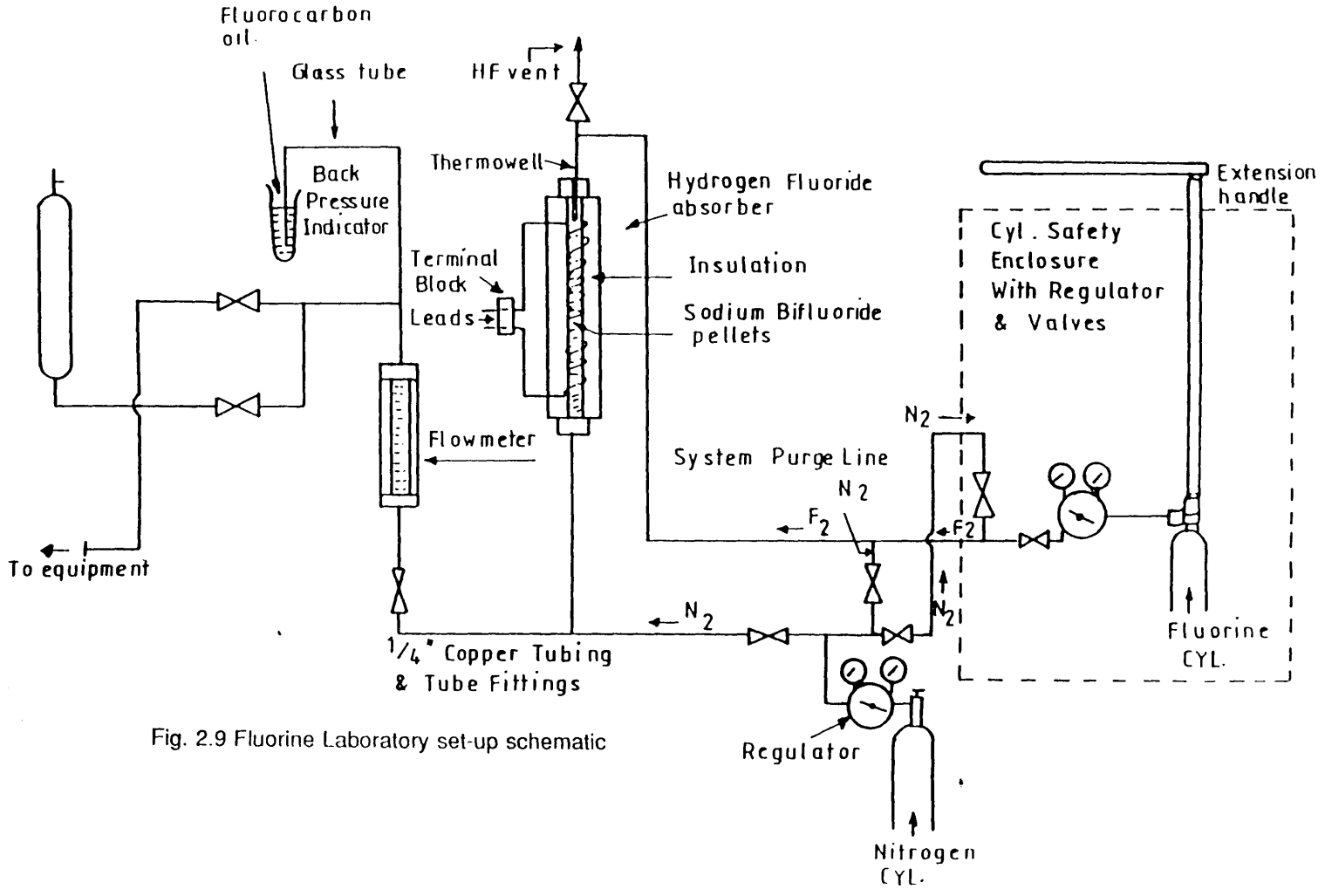


Fig. 2.9 Fluorine Laboratory set-up schematic

dry ice/dichloromethane slush baths. Meanwhile, the fluorine cylinder was opened, and the cylinder head pressure gauge was adjusted to 40 psi. Fluorine gas diluted with nitrogen gas was passed through the system, the ratio F:N=1:2 by volume. The products were collected in the trap G and the reaction was finished after about one hour. Testing for F_2 at the exhaust of the apparatus was accomplished by the use of potassium iodide/starch indicator paper.

After the reaction was complete, the main valve, 6, of the fluorine cylinder was closed. When the pressure reading in the pressure gauge of the cylinder dropped to zero, valves 5 and 4 were closed, and the apparatus was purged with nitrogen gas for about 15 minutes.

The glass apparatus was detached by sealing at point H, separated from socket D (Fig. 2.8), and immediately re-attached to a vacuum line to be evacuated, the products being frozen in liquid nitrogen. The product tungsten hexafluoride, WF_6, or molybdenum hexafluoride, MoF_6, was purified by trap-to-trap vacuum distillation firstly from the trap G to F, and then from F to E. In order to obtain a pure product, a slow distillation was necessary at this step, from -80^0C (dry ice/dichloromethane slush bath) to -196^0C (liquid nitrogen). The main impurity was $MoOF_4$ or WOF_4, which were less volatile. Finally, the product was sealed in E at the point O and stored at liquid nitrogen temperature until required.

2:5c Preparation and Purification of N_2O_4

The preparation method for dinitrogen tetroxide was by means of the thermal decomposition of lead nitrate, $Pb(NO_3)_2$ (Riedel-De Huen A.G.). The apparatus was a Pyrex glass reactor which is shown in Fig. 2.10.

Lead nitrate (approx. 9 g) was loaded in the reaction tube, and suitable amounts of P_2O_5 were loaded in the traps A, B, and C. The apparatus was set up as in Fig. 2.10, and was dried under vacuum at 25^0C for at least two hours. Trap A was cooled by a liquid nitrogen-carbon tetrachloride slush bath (-20^0C) and trap B was kept in -80^0C using a dry ice/dichloromethane bath, meanwhile, the lead nitrate, $Pb(NO_3)_2$, was gently heated by using a gas/oxygen torch to achieve decomposition. The dinitrogen tetroxide prepared was collected in the trap B, moisture and nitric acid resulting from the decomposition of lead nitrate, $Pb(NO_3)_2$, were retained in the trap A. After all the lead nitrate, $Pb(NO_3)_2$, had decomposed, the stopcock was closed, and the trap B was cooled at -20^oC using a liquid nitrogen-carbon tetrachloride slush bath and trap C was cooled at -80^oC using dry ice/dichloromethane. Purification of dinitrogen tetroxide, N_2O_4, prepared was carried out by trap-to-trap distillation over P_2O_5, and finally the dinitrogen tetroxide, N_2O_4 was condensed into a stainless steel pressure vessel (Hoke, 90 cm^3) and stored until required.

The infrared spectrum of dinitrogen tetroxide prepared was

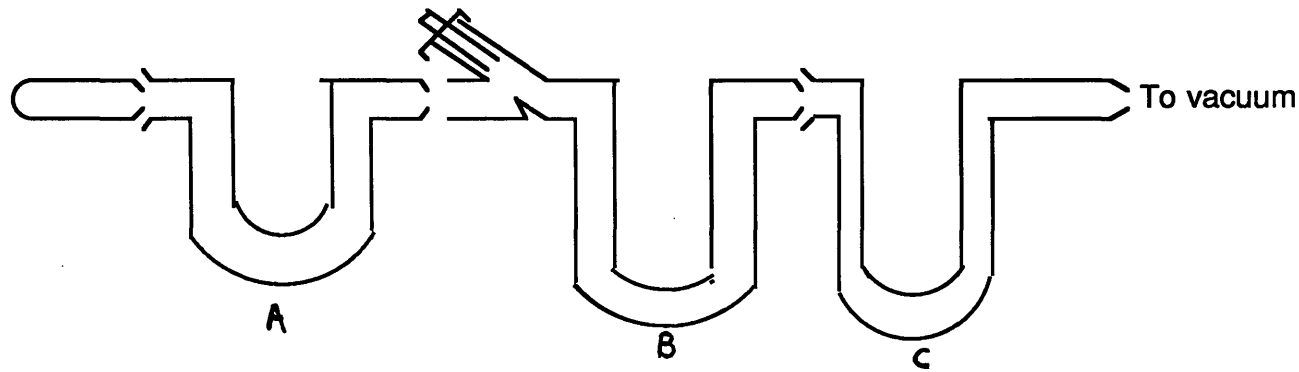


fig. 2.10 apparatus for preparation of dinitrogen tetroxide.

recorded using a gas cell, and is presented in Table 2.1. No trace of nitric acid was found.

2:5d Preparation and Purification of Carbonyl Fluoride

Carbonyl fluoride was prepared by the reaction between carbonyl chloride and sodium fluoride in acetonitrile.

Acetonitrile (30 cm^3) and carbonyl chloride (3.0g, 30.4mmol) were condensed into a stainless steel pressure vessel (300 ml) containing sodium fluoride (6g, 360mmol). The reaction mixture was kept at 20^0C for about 36 hours. Fractionation of the volatile components gave carbonyl fluoride. It was purified by trap-to-trap distillation at -80^0C and stored in a stainless steel pressure vessel until required.

2:5e Activation of CsF and KF

Caesium fluoride and potassium fluoride were activated by the reaction with carbonyl fluoride (method of preparation in section 2.5d) or hexafluoroacetone in acetonitrile and then thermal decomposition of its hexafluoroacetone or carbonyl fluoride adducts.[128] Previous work has shown that the surface areas of the fluorides are significantly increased[128,129] after activation and the reactivity of the fluorides are enhanced.[130]

Caesium fluoride (3g, 20mmol, B.D.H. Optran grade), or

Table 2.1

Infrared Spectrum (cm^{-1}) of Dinitrogen Tetroxide

This work	Literature [127]	Assignment
	3440(w)	$\upsilon_5 + \upsilon_9$ Comb.
	3111(m)	$\upsilon_1 + \upsilon_9$ Comb.
2920(m)	2971(m)	$\upsilon_5 + \upsilon_{11}$ Comb.
	2747(w)	$\upsilon_{11} + 2\upsilon_{12}$ Comb.
2620(w)	2630(m)	$\upsilon_1 + \upsilon_{11}$ Comb.
	2579(w)	$\upsilon_8 + \upsilon_{11}$ Comb.
	2124(w)	$\upsilon_1 + \upsilon_{12}$ Comb.
	1937(w)	$\upsilon_{11} + \upsilon_8$ Comb.
1750(s)	1748(s)	υ_9 NO str.
1616(s)		?
	1495(w)	$\upsilon_9 - \upsilon_3$ Comb.
1260(s)	1262(s)	υ_{11} NO str.
750(s)	750(v.s.)	υ_{12} def.
	695(m)	$\upsilon_3 + \upsilon_7$ Comb.
	429(s)	υ_7 NO_2 wag.
	381(m)	υ_{10} NO_2 rock.

w: weak; m: medium; s: strong; v.s. : very strong.

potassium fluoride were thoroughly ground using an agate pestle and mortar in the inert atmosphere glove box and loaded in a stainless steel pressure vessel (Hoke.Inc.) containing four stainless steel ball-bearings.The vessel was attached to a vacuum line and evacuated. Acetonitrile(5 cm^3) and carbonyl fluoride, COF_2 (33mmol), or hexafluoroacetone $(CF_3)_2CO$ (33mmol) were condensed into the vessel by vacuum distillation. The vessel was allowed to warm to room temperature and shaken overnight (about 12 hours). After that, acetonitrile and excess carbonyl fluoride, or hexafluoroacetone were removed, and the vessel was heated at 120^0C for sixteen hours by means of an electric heater. The resulting solid was off-white in colour. It was transferred to the glove box, ground and stored in a sealed glass vessel until required.

2:5f Preparation of Nitrosyl Fluoride[13 1]

The preparation method for nitrosyl fluoride was very simple, the direct reaction between dinitrogen tetroxide and activated potassium fluoride, or activated caesium fluoride (for the activation method see section 2:5e).

Dinitrogen tetroxide (4mmol) was condensed in a stainless steel pressure vessel (Hoke, 90 cm^3) which contained a large excess of activated potassium fluoride or caesium fluoride. The bomb was allowed to warm slowly to room temperature, only 30 minutes were required for the reaction. After that, the bomb was cooled to -80^0C using a dry ice/dichloromethane bath to retain unreacted N_2O_4, and FNO prepared was immediately

removed and used. Based on the initial pressure of N_2O_4, the yield of FNO was 50%.

2:5g Preparation of Nitrosonium Tetrafluoroborate

Nitrosonium tetrafluoroborate was prepared by homogeneous gas phase reaction between nitrosyl fluoride and BF_3 in a one-limb Pyrex glass vessel. A mixture of FNO (4 mmol) and excess BF_3 (8 mmol) was condensed into a previously evacuated and flamed out reaction vessel. The mixture was allowed to warm very slowly to room temperature, the reaction was very fast and a white solid was obtained. After removal of excess reactants the product was transferred to the glove box and stored in an ampoule sealed under vacuum until required. The infrared spectrum of the solid prepared contained bands at 2340 cm^{-1}, 1100-1020 cm^{-1} (strong, broad) and 520 cm^{-1}. They were assigned to the stretching vibration of NO^+ and to the υ_3 and υ_4 vibrational modes of BF_4^-.

2:5h Preparation of Nitrosonium Heptafluorotungstate

Nitrosonium heptafluorotungstate(VI) was prepared by homogeneous gas phase reaction between nitrosyl fluoride and tungsten hexafluoride. Excess WF_6 (5mmol) was distilled into a previously flamed out and evacuated one-limb reaction vessel by vacuum distillation and the FNO was then condensed into the vessel. The mixture was allowed to warm very slowly to room temperature. The reaction was very fast and a white solid was

obtained. After removal of excess reactants, the product was transferred to the dry glove box and stored in an ampoule sealed under vacuum until required. The infrared spectrum of the solid prepared contained bands at 2330 cm^{-1} and 620 cm^{-1}. They were assigned to the vibration of NO^+ and to the υ_3 vibrational mode of WF_7^- in pentagonal bipyramidal symmetry (D_{5h}),[132] respectively.

2:5i Preparation of $NOMoF_6$[106]

Acetonitrile ($5cm^3$) was distilled into one limb of a previously flamed out and evacuated double-limb reaction vessel. Molybdenum hexafluoride (1 mmol) and nitric oxide (1.5 mmol) were distilled in turn into the reaction vessel and the reaction mixture was allowed to warm slowly to room temperature. An orange solid was isolated from the resulting solution after removal of volatile materials. Its infrared spectrum contained bands at 620 (υ_3) and 240 (υ_4) cm^{-1} corresponding to MoF_6^- and one band at 2340 cm^{-1} assigned to υ(NO) of NO^+. The orange solid was thus identified as nitrosonium hexafluoromolybdate(v).

2:5j Preparation of Nitrosonium Hexafluorouranate[106]

Acetonitrile ($5cm^3$) was distilled into one limb of a previously flamed out and evacuated double-limb reaction vessel. Uranium hexafluoride (British Nuclear Fuels Ltd. purified by trap-to-trap distillation) and nitric oxide, NO (1.5 mmol) were distilled into the reaction vessel. The vessel was allowed to warm slowly to room

temperature. A pale green solid was isolated from the resulting pale green solution after removal of the volatile materials. The infrared spectrum of the product prepared contained bands at 520 (υ_3) and 2320 cm^{-1} assigned to UF_6^- and NO^+ respectively.

2:6 Quantitative Analysis

Quantitative analysis of the compounds prepared was carried out by various methods. Analyses for the C, H, and N elements were made by the Microanalytical Laboratory, Department of Chemistry, Glasgow University, using Elemental Analyser-MOD 1106, Molybdenum was determined by atomic absorption spectroscopy and Ln^{3+} metal ions were analysed by EDTA titration. Brief description of methods used are given below.

2:6a Atomic Absorption Spectroscopy for Analysis of Molybdenum

Atomic absorption spectroscopy is a very useful technique for the analysis of many elements. The method is based on the absorption of radiation by an atom in the uv-visible region of the spectrum. The conversion of the element to its atomic state is necessary and the normal way of producing atoms is to use a reducing environment, such as the N_2O-C_2H_2 flame. Although the atoms of various elements can undergo many electronic transitions which result in a series of sharp lines forming a spectrum, the atom of each element has a characteristic spectrum.

The energy change ΔE of an electronic transition within an atom follows Planck's law:

$$\Delta E = h\upsilon \qquad (2\text{-}5)$$

where h is Planck's constant and υ is the frequency(Hz).

When a parallel beam of continuous radiation of intensity I_0 passes through a flame containing the sample in the form of atomic vapour, only part of the radiation is transmitted. This can be expressed by the Beer-Lambert law as follow:

$$A = \log I_0/I = \varepsilon LC \qquad (2\text{-}6)$$

where A is absorbance;

C is the concentration of the analyte atoms in the flame (number of atoms per cm^3);

L is path lengh of absorption cell (cm);

ε is an atomic absorptivity for a given system.

There is a linear relationship between absorbance and concentration when ε and L are constant.

2:6a$_1$ Sample Preparation

A sample of the compound (~15 mg) for atomic absorption analysis was transferred to a frangible ampoule in a dry glove box. The frangible ampoule was then attached to a vacuum line, evacuated, and sealed by using a gas/oxygen torch. The external

surface of the ampoule was washed with acetone and dried entirely before weighing precisely. The ampoule was broken over a filter funnel leading to a conical flask ($100cm^3$) in which the contents of the ampoule were quantitatively transferred. The ampoule and funnel were washed with Analar HNO_3 ($5cm^3$) to remove any residues. Finally distilled water ($10cm^3$) was used to rinse the ampoule and funnel, the washings being led to the conical flask via the funnel. The resulting solution was digested just below its boiling point for about 0.5 hour, and then cooled. It was quantitatively transferred to a volumetric flask ($100cm^3$) and distilled water was added to bring the total volume of the solution to $100cm^3$. The broken frangible ampoule and pieces of glass were weighed again to obtain the original sample weight. A part of this solution ($5cm^3$) was diluted to $100cm^3$ and, at this stage, Na_2SO_4 (0.1% w/v) was added to minimise interference effects in the C_2H_2-N_2O flame.

Calibration was carried out by serial dilution of the appropriate "Spectrosol" standard molybdenum solution in the range of 0-40μg/ml. Standard solutions were also matrix matched with respect to HNO_3 and Na_2SO_4 concentrations.

The absorbance of each sample solution was obtained using a Perkin-Elmer 306 atomic absorption spectrophotometer, with a nitrous oxide/ acetylene flame. The manufacturer's standard operating conditions were used, as listed in Table 2.2.

The solution concentration of the unknown sample was

Table 2.2
Operating Conditions for Molybdenum

Wavelength	313.3 mm
Slit	0.7 mm
Flame	N_2O-C_2H_2
Burner length	5 cm
Linear range	0 - 50 μ g/cm^3
Source	Hollow cathod H "cathode " lamp
Matrix	5% HNO_3 + 0.1%w/v Na_2SO_4
Signal mode	10 s integration

obtained from the absorbance-concentration plot. The values in $\mu g/cm^3$, thus obtained, were then converted to unit/percentage using the following fomula:

$$Wt\% = [\text{concentration}(\mu g/cm^3) \times \text{sample volume} \times \text{dilution factor} \times 10^{-4}]/Wt$$

Concentration: value in $\mu g/cm^3$ read from graph;
Sample volume: 100 cm^3;
Dilution factor: 10.

2:6b EDTA Titration

The lanthanide ions were determined by the method described by Lyle and Rahman,[133] that is titration with EDTA (0.01mol dm^{-3}) using xylenol orange, 1% in 1:1 (w/v) ethanol-water mixture, as an indicator and HOAc + NaOAc solution (pH=5) as the buffer solution.

2:6b$_1$ Test Solution Preparation

Lanthanum metal powder (0.1389 g) was weighed precisely by means of the analytical balance and dissolved in 0.1 mol dm^{-3} HOAc solution (10 cm^3). It was then transferred to a volumetric flask and distilled water was used to bring it to a total volume of 100 cm^{-3}. A part of this solution (10 cm^3) was transferred to another volumetric flask and diluted to 100 cm^3 using distilled water. The concentration of this solution was 0.1000 mmol dm^{-3}.

2:6b_2 Sample Solution Preparation

A sample of a compound for EDTA titration was transferred to a frangible ampoule in the inert atmosphere glove box. It was attached to a vacuum line, evacuated, and the ampoule was sealed by a gas/oxygen torch. the external surface of the ampoule was washed with acetone and dried entirely before weighing it precisely. The ampoule was broken and the contents of the ampoule was collected in a small beaker. The broken ampoule was washed with 5 ml of Analar HNO_3 to remove any residues. Finally the distilled water (~10 cm^3) was used to rinse the broken ampoule, the washings being led to the beaker. The resulting solution was digested just below its boiling point for about 0.5 hour, and then cooled. The procedure that followed depended on the nature of the anion present.

(1) Salts containing anion PF_6^-: A aqueous NaOH solution was used to adjust the pH of sample solution until precipitation occurred. It was left for approximately 5 hours so that the precipitation was complete. The precipitate was separated by means of the sintered glass filter and dissolved in the concentrated HNO_3. Finally the solution was adjusted to pH=5 using aqueous NaOH.

(2) Salts containing WF_6^- or MoF_6^-: The concentrated HNO_3 (~10cm^3) was added to precipitate WO_3 or MoO_3 and it was then left for about 5 h until the precipitation was complete. The solution phase was separated using the sintered glass filter and adjusted to pH=5 using aqueous NaOH.

CHAPTER THREE

REACTIONS OF THE LANTHANIDE METALS (La, Nd, Eu and Tm) WITH THE HEXAFLUORIDES (UF_6, MoF_6 and WF_6) IN MeCN

3:1 Introduction

The reactions between lanthanide metals and high oxidation state fluorides, such as UF_6, MoF_6 and WF_6 in acetonitrile have not been reported in the literature, although the behaviour of UF_6, MoF_6, and WF_6, towards transition metals and post-transition metals in acetonitrile has been well-investigated.[76,77] The oxidation of lanthanide metals by the hexafluorides of uranium, molybdenum and tungsten in acetonitrile is described in this chapter. Lanthanum(La), neodymium(Nd), europium(Eu) and thulium(Tm) were chosen for this work, the reason being that the first three are the "light earths", and are thought of as being rather reactive. Thulium belongs to the "heavy earths" and its reactivity is less than those of the other three lanthanide metals, however, it was chosen in order to compare with the reactivity of the first three "light earth" elements.

3:2 Results

3:2:1 Study of the Reactions between Lanthanide Metals (La, Nd, Eu, and Tm) and Uranium Hexafluoride in Acetonitrile

It was found that lanthanide metals (La, Nd, Eu, and Tm) did not react with uranium hexafluoride in acetonitrile, although uranium hexafluoride was reduced by acetonitrile.

In previous work[113] it was found that uranium hexafluoride

did not react with nickel, cobalt or zinc, but it reacted with solvent MeCN. The reaction between uranium hexafluoride and acetonitrile has been well-investigated by J. A. Berry in this Department.[134] It was proposed that the fluorination and polymerization of acetonitrile accompanied the reduction of uranium hexafluoride. The course of the reactions between the four lanthanide metals and uranium hexafluoride in acetonitrile was followed by electronic spectroscopy. Spectra were recorded every two hours until polymerization of solvent was apparent. Comparison with the spectra of UF_6 in MeCN recorded at the same time indicated that the electronic spectra of the UF_6 + NCMe mixture were almost identical with those of mixture comprising Ln + UF_6 + MeCN. A group of bands clustered at ca. 1370 nm was observed in both cases and the intensities of these bands increased with time. This group of bands was assigned to a f-f transition of UF_5 generated from the reduction of UF_6 by acetonitrile from comparison with Berry's work.[134] The observations indicated that the reaction involved UF_6 and MeCN only. Lanthanide metals were not involved.

3:2:2 Investigation of the Reactions between MoF_6 and Lanthanum or Thulium in Acetonitrile

The reactions of molybdenum hexafluoride with lanthanum, or thulium powder metal in acetonitrile were attempted, but proved unsuccessful.

3:2:3 Investigation of the Reactions between WF_6 and Neodymium or Thulium in Acetonitrile

The reactions between neodymium, or thulium metal and tungsten hexafluoride in acetonitrile have been attempted, but no evidence of reaction was found.

3:2:4 Preparation of the Solids $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Ln(NCMe)_3][WF_x]_3$ (Ln=La, Eu; x=6, or 7) from the Oxidation of La, Nd, or Eu Metals by MoF_6, or WF_6 in MeCN

The attempted reaction between molybdenum hexafluoride and neodymium metal powder in acetonitrile was unsuccessful, but the reactions between molybdenum hexafluoride and europium metal powder, or neodymium metal ingot (freshly cut into small pieces in the glove box) in acetonitrile at room temperature produced pale-yellow solid compounds. The reactions between lanthanum, or europium metals and tungsten hexafluoride under same conditions also gave pale-yellow solid compounds. These four compounds were sensitive to moisture, and the four reactions were very slow. When molybdenum hexafluoride was used, the reactions were difficult to perform owing to contamination by the slow polymerization of acetonitrile by the molybdenum hexafluoride. The yields were small, ~10 mg of solid compound were obtained each time from the reactions. The infrared spectra of the four compounds showed the presence of coordinated acetonitrile, and also

indicated the presence of the MoF_6^- anion or the WF_6^- anion (Table 3.1). A sharp intense band at $2295cm^{-1}$ (or $2280cm^{-1}$) was assigned to the fundamental C≡N stretch and a weaker band at $2330cm^{-1}$ (or $2320cm^{-1}$) was assigned to a combination of the C-C stretch and the CH_3 deformation modes. The intensity of the latter band arises from Fermi resonance between the combination band and the C≡N stretching vibration, owing to both the combination band and the stretching vibration have A_1 symmetry. The CH_3 rock (υ_7) was assigned to a band at $1030cm^{-1}$ (or $1020cm^{-1}$). A band assigned to the C-C stretch (υ_4) was found at 950 cm^{-1} (or $940cm^{-1}$). The bands absorbing at 650 and $250cm^{-1}$ (or $240cm^{-1}$) were assigned to $MoF_6^-(\upsilon_3)$ and $MoF_6^-(\upsilon_4)$, respectively. In the case of WF_6 reactions, a band at $600cm^{-1}$ was assigned to a $WF_6^-(\upsilon_3)$ and a band at $705cm^{-1}$ was considered to arise from the anion WF_7^-.[76] The reason for the presence of WF_7^- was that a fluoride ion transfer reaction can occur in parallel with the oxidation of lanthanide metals by WF_6 in acetonitrile. A similar situation was found earlier to accompany the oxidation of a number of the metals in acetonitrile by WF_6.[76,113] The following reactions were proposed to explain the occurrence of WF_7^-.

$$WF_6\ (solv.) + e^- \text{--------} > WF_6^-\ (solv.) \qquad (3\text{-}1)$$

$$WF_6(solv.) + WF_6^-(solv.) = WF_7^-(solv.) + WF_5(solv.) \qquad (3\text{-}2)$$

On the basis of the analytical results for the elements carbon,

Table 3.1

Infrared Spectra (cm^{-1}) of the Solid Salts

A	B	C	D	Assignment
2320(m)	2330(s)	2320(s)	2320(s)	Comb.$CH_3CN(\upsilon_3+\upsilon_4)(A_1)$
2280(s)	2295(s)	2295(s)	2280(s)	C≡N Str. (υ_2) (A_1)
1020(s)	1030(m)	1020(s)	1020(s)	CH_3 Rock (υ_7) (E)
955(w)	950(m)	940(m)	940(m)	C-C Str. (υ_4) (A_1)
705(m)			705(m)	WF_7^-
600(s)			600(s)	WF_6^- (υ_3)
	650(s)	650(s)		MoF_6^- (υ_3)
	250(s)	240(s)		MoF_6^- (υ_4)

A=$[La(NCMe)_3][WF_x]_3$; B=$[Nd(NCMe)_3][MoF_6]_3$;

C=$[Eu(NCMe)_3][MoF_6]_3$; D=$[Eu(NCMe)_3][WF_x]_3$. x=6 or 7.

s: strong; m: medium; w: weak.

hydrogen, nitrogen, molybdenum, lanthanum, neodymium and europium (Table 3.2), the stoichiometries of the two compounds obtained using MoF_6 were consistent with the formulations $[Nd(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][MoF_6]_3$. The stoichiometries of the two solids obtained using WF_6 were consistent with the formulations $[La(NCMe)_3][WF_6]_3$ and $[Eu(NCMe)_3][WF_6]_3$, however, they were also close to the formulations $[La(NCMe)_3][WF_7]_3$ and $[Eu(NCMe)_3][WF_7]_3$. Therefore, these two solids were regarded as a mixture of $[Ln(NCMe)_3][WF_6]_3$ and $[Ln(NCMe)_3][WF_7]_3$ (Ln=La, Eu). These results were consistent with the lanthanides being in the +3 oxidation state. It also appeared that the coordination number of the cation by acetonitrile was three in the compounds. This was in contrast to many other complexes of the lanthanides, in which the coordination number of the metal is normally more than six, as described in chapter one. A possible explanation is that coordinated acetonitrile molecules are lost from the coordination sphere during the course of the compounds being isolated from the reaction solution, owing to the weak coordinating ability of acetonitrile. It has been reported[76] that one of the coordinated acetonitrile molecules is lost from the cation $[Co(NCMe)_6]^{2+}$ generated in the reaction between cobalt metal and WF_6 in MeCN during isolation of the solid. It is also believed that coordinated acetonitrile is lost from iron(II) during isolation of the solid $[Fe(NMe_3)(NCMe)_4][PF_6]_2$.[135] It is possible that there is an interaction between the cation and the hexafluorometallate(V) anion in the solid state, so that the coordination number in the solid compounds $[Ln(NCMe)_3][MoF_6]_3$ (Ln=Nd, or Eu) and $[Ln(NCMe)_3][WF_x]_3$ (x=6,

Table 3.2

Analytical Data[a] for Lanthanide(III) Complexes

Complex	Colour	Analysis(%)				
		C	H	N	Ln[b]	Mo
$[Nd(NCMe)_3][MoF_6]_3$	pale yellow	7.98 (8.03)	1.04 (1.01)	4.79 (4.69)	15.90 (16.08)	31.60 (32.08)
$[Eu(NCMe)_3][MoF_6]_3$	pale yellow	8.14 (7.90)	1.08 (1.00)	4.55 (4.65)	17.03 (16.79)	32.35 (31.81)
$[Eu(NCMe)_3][WF_6]_3$ or $[Eu(NCMe)_3][WF_7]_3$	pale yellow	6.25 (6.17) [5.90]	0.85 (0.78) [0.74]	3.77 (3.60) [3.43]	12.88 (13.00) [12.40]	—
$[La(NCMe)_3][WF_6]_3$ or $[La(NCMe)_3][WF_7]_3$	pale yellow	6.23 (6.24) [5.94]	0.84 (0.79) [0.75]	3.62 (3.64) [3.47]	11.95 (12.02) [11.46]	—

a Required values in $[Ln(NCMe)_3][MF_6]_3$ (M=Mo or W) are given in parentheses and required values in $[Ln(NCMe)_3][WF_7]_3$ are given in square brackets.

b Ln=La, Nd or Eu.

or 7) is greater than three, but no proof for this was obtained.

The magnetic susceptibilities, $\chi^{corr.}10^6$ c.g.s. and magnetic moments, $\mu_{eff.}$ determined for the four solid compounds at 298K are given in Table 3.3. The paramagnetic properties of the compounds can arise from contributions due to unpaired f electrons at the central lanthanide ions and the d^1 configuration of M(V) in the anions MF_6^-(M=Mo, or W). In the compound containing La(III), the paramagnetism was due to the unpaired d electron at the W(V) of the anion WF_6^-. Generally, the spin-only magnetic moment value for a d^1 configuration is μ=1.73 BM.

The simple idea of the magnetic behaviour of the d block elements which relates paramagnetism directly to the number of unpaired electrons is very useful, but it is satisfactory only in the first transition series and imperfect in the second and third rows. Lower values of the magnetic moments are obtained for the second and third series due to spin-orbit coupling which is often greater in the 4d and 5d compounds. For example, the magnetic moments of some hexafluoromolybdate(V) and hexafluorotungstate(V) salts, such as $[Ag(NCMe)_2][MoF_6]$, $[Ag(py)_4][MoF_6]$, $[Ag(py)_4 \cdot NCMe][MoF_6]_3$ and $[Ag(NCMe)_2][WF_6]$ have been reported,[136] and are, respectively, 1.00, 0.99, 0.93 and 0.65 BM per M^V atom(M=Mo, or W) at 295K. The literature values of the magnetic moments of the free neodymium(III) and europium(III) ions are, respectively, in the ranges 3.44-3.65 and 3.32-3.54 BM.[7] In the compound $[La(NCMe)_3][WF_x]_3$ (x=6, or 7), the measured value of the magnetic moment was less than the

Table 3.3

Corrected molar magnetic susceptibilities, $\chi^{corr.}$ and effective magnetic moments, $\mu_{eff.}$, of the hexafluoride salts of the lanthanides(III) at 298K

Complexes	$10^6 \chi^{corr.}$ (c.g.s.)	$\mu_{eff.}$(BM)
$[Nd(NCMe)_3][MoF_6]_3$	10,950	5.13
$[Eu(NCMe)_3][MoF_6]_3$	10,290	4.97
$[Eu(NCMe)_3][WF_x]_3$	11,580	5.28
$[La(NCMe)_3][WF_x]_3$	1,052	1.59

x=6 or 7.

simple combination expected from three WF_6^- anions, hence the occurrence of WF_7^-, which is diamagnetic, might be responsible for magnetic moment being low. In the compound $[Eu(NCMe)_3][WF_x]_3$ (x=6, or 7), the measured value of the magnetic moment was consistent with the simple combination of the value for free Eu(III) ion and the values for three WF_6^-; this showed that there was possibly little WF_7^- in the solid so that its influence for the paramagnetic property of the solid was small. In the two compounds $[Nd(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][MoF_6]_3$, the measured values of the magnetic moments were also less than that expected from the simple combination of the values for free Nd(III), or Eu(III) ions and the value for three MoF_6^- anions. It is possible to envisage an interaction between the cation and the anion in the compounds so that their magnetic moments are decreased. No experimental work was undertaken to test this hypothesis and a more detailed study would be required.

In the electronic spectra of the four solid compounds that were prepared, a strong band in the ultra-violet region was observed. The positions of $\nu_{max.}$ and molar absorptivities are given in Table 3.4. Owing to f-f transitions being Laporte forbidden and very weak, the molar absorptivities[137] are ε=0.5 $dm^3mol^{-1}cm^{-1}$. The bands observed here have not been regarded as being due to f-f transitions. In $[La(NCMe)_3][WF_x]_3$, (x=6, or 7), the band was possibly due to charge transfer, and in the other cases, the bands possibly were due to either charge transfer or an allowed 4f-5d transition.

Table 3.4
Electronic spectra of lanthanide(III) complexes

Complex	ν_{max} (cm^{-1})	Assignments
$[Nd(NCMe)_3][MoF_6]_3$	37,300 (ε =91)	4f-5d or C. T.
$[Eu(NCMe)_3][MoF_6]_3$	29,100 (ε =77)	4f-5d or C. T.
$[Eu(NCMe)_3][WF_x]_3$	29,200 (ε =80)	4f-5d or C. T.
$[La(NCMe)_3][WF_x]_3$	32,800 (ε =84)	C. T.

C. T. - charge transfer.
x=6 or 7.
The unit of ε are $dm^3\ mol^{-1}cm^{-1}$.

From the combination of the elemental analyses, infrared spectra and the magnetic moments of the solid compounds prepared, the reaction between the lanthanide metals and molybdenum hexafluoride, or tungsten hexafluoride in acetonitrile can be described by the equation.

$$Ln(s) + 3MF_6\,(solv.) \xrightarrow{MeCN} [Ln(NCMe)_y]^{3+} + 3MF_6^{-}(solv.)$$
$$\longrightarrow [Ln(NCMe)_3][MF_x]_3(s) \qquad (3\text{-}3)$$

Ln=Nd, or Eu; x=6 for M=Mo. Ln=La, or Eu; x=6, or 7 for M=W.

3:3 Conclusion

The reactions occurring between the lanthanide metals (La, Nd, Eu and Tm) and the hexafluorides UF_6, MoF_6 and WF_6 in acetonitrile at room temperature are given below.

Table 3.5
Survey of the Reactions Occurring between the Lanthanide Metals and the Hexafluorides

	La	Nd	Eu	Tm
UF_6	no	no	no	no
MoF_6	no	re.	re.	no
WF_6	re.	no	re.	no

re.-reaction; no-no reaction.

3:4 Experimental

Lanthanide metal powder, purity 99.9% (Johnson Matthey); neodymium metal powder, or ingot, purity 99.9% (Johnson Matthey); europium metal powder, purity 99.9% (Cambrian Chemical Ltd.); thulium metal powder, purity 99.9% (Halewood Chemicals Ltd.) were used as supplied and stored in the nitrogen filled glove box. The high oxidation state fluorides WF_6, MoF_6 (method of preparation described in chapter two) and UF_6 (British Nuclear Fuels Ltd.), were purified by low temperature trap-to-trap distillation over activated NaF and stored over NaF at liquid nitrogen temperature. Acetonitrile (Rathburn Chemicals Ltd., HPLC Grade S) was purified according to the method described in chapter two. Weighing of the chemicals inside the glove box was accomplished by means of an electronic balance (Sartorius Model 1205 MP) with an estimated error of $\pm$ 0.004 g.

3:4:1 Reactions of Lanthanide Metals (La, Nd, Eu, and Tm) with Uranium Hexafluoride in Acetonitrile

When MeCN and UF_6 were in turn distilled into a dry evacuated double-limb reaction vessel containing one of the lanthanide metals (1 mmol) used, the reaction mixture became yellow even at low temperature. The yellow colour changed rapidly to green and after a few hours became brown as a result of solvent polymerization.

3:4:2 Reactions of Lanthanum or Thulium with Molybdenum Hexafluoride in Acetonitrile

A double-limb Pyrex glass reaction vessel which had been flamed out and evacuated was loaded with lanthanum or thulium metal (0.5 mmol) in a glove box . The vessel was attached to the vacuum line and evacuated. Acetonitrile($5cm^3$) and molybdenum hexafluoride(15 mmol) were in turn distilled into the reaction vessel .The mixture was allowed to warm up slowly to room temperature and left to stand for several days, but there was no evidence of reaction in either case. The colour of the mixture did not change and, after removal of the volatile materials from the reaction vessel, no solid was isolated. When MoF_6 was used, special care was taken to avoid the polymerization of the solvent. It was found that if the reaction mixture was frozen and degassed several times during the course of the reaction, the polymerization of solvent by MoF_6 could be delayed for a period of time(approx. three days), otherwise, the polymerization of solvent was very fast, especially when a large excess of molybdenum hexafluoride was used.

3:4:3 Oxidation of Neodymium Metal by Molybdenum Hexafluoride in Acetonitrile

In this reaction, both neodymium metal ingot and neodymium metal powder were used. In the case of the metal powder, no matter what quantity of molybdenum hexafluoride was used, there was no evidence of reaction. Using neodymium metal ingot,

a reaction did occur providing the metal ingot was cut into very small pieces, the appearance of the surface of the pieces were bright and appeared to be free of oxidized film. These small pieces of Nd metal (1 mmol) were loaded in a previously flamed out and evacuated double-limb reaction vessel in the glove box. The reaction vessel was attached to the vacuum line and evacuated. Acetonitrile ($5cm^3$) and molybdenum hexafluoride (10 mmol) were added in turn to the reaction vessel by vacuum distillation. The reaction mixture was allowed to warm up slowly to room temperature and was shaken for about three days. During the course of the reaction, it was necessary to freeze the reaction mixture and evacuated it several times to prevent the slow polymerization reaction between the acetonitrile and molybdenum hexafluoride. A pale yellow solution was formed and when the unreacted reactants and solvent were removed, a small quantity of pale yellow solid compound was isolated. The solid compound obtained was very unstable and sensitive to moisture and was kept in a sealed glass ampoule and stored at low temperature.

On the basis of the infrared spectrum and the elemental analysis for the C, H, N, Nd and Mo (Table 3.1 and 3.2), the solid compound prepared was consistent with the formulation $[Nd(NCMe)_3][MoF_6]_3$. The magnetic moment of the compound was determined to be 5.13 BM at 298 K (Table 3.3) and its electronic spectrum was also recorded(Table 3.4), and showed a strong band at 37,300 cm^{-1}.

3:4:4 Oxidation of Europium Metal by Molybdenum Hexafluoride in Acetonitrile

Europium metal (0.5 mmol) was added to a dry evacuated double-limb reaction vessel in the glove box. The reaction vessel was attached to the vacuum line and evacuated. Acetonitrile ($5cm^3$) and molybdenum hexafluoride (10 mmol) were distilled into the double-limb reaction vessel under vacuum. The reaction mixture was allowed to warm up to room temperature and was shaken for two days. During the reaction the mixture was often frozen and pumped to prevent polymerization of acetonitrile by molybdenum hexafluoride. The solution was pale yellow. A small quantity of pale yellow solid was isolated from the resulting solution.

On the basis of its infrared spectrum and elemental analysis for C, H, N, Eu and Mo (Table 3.1 and 3.2), the stoichiometry of the solid compound was consistent with the formulation $[Eu(NCMe)_3][MoF_6]_3$. The magnetic moment of the compound was determined to be 4.97 BM at 298K (Table 3.3) and a strong band at 29,100 cm^{-1} was observed in its electronic spectrum (Table 3.4).

3:4:5 Reaction of Neodymium or Thulium Metal with Tungsten Hexafluoride in Acetonitrile

Neodymium, or thulium metal was added into a previously flamed out and evacuated double-limb reaction flask.

Acetonitrile(5cm^3) and tungsten hexafluoride(15 mmol) were in turn added into the reaction flask. The reaction mixture was allowed to warm up to room temperature and was shaken for four days. The colour of the solution mixture did not change and unreacted metal was isolated by removal of the volatile material.

3:4:6 Oxidation of Lanthanum Metal by Tungsten Hexafluoride in Acetonitrile

Lanthanum metal powder(0.5 mmol) was added into a dry evacuated double-limb reaction vessel in the glove box. The double-limb vessel was attached to the vacuum line and evacuated. Acetonitrile(5 cm^3) and tungsten hexafluoride (10 mmol) were in turn distilled into the reaction vessel. The mixture was allowed to warm up to room temperature and was shaken for three days. The colour of the solution mixture became pale yellow. A small quantity of pale yellow solid was isolated after removal of the unreacted oxidizing agents and solvent. On the basis of its infrared spectrum and elemental analysis for the C, H, N and La(Table 3.1 and 3.2), the solid was consistent with being a mixture of $[La(NCMe)_3][WF_6]_3$ and $[La(NCMe)_3][WF_7]_3$. Its magnetic moment was determined to be 1.59BM at 298K (Table 3.3) and a strong band at 32,800 cm^{-1} was observed in the electronic spectrum of the solid.

3:4:7 Oxidation of Europium Metal by Tungsten Hexafluoride in Acetonitrile

A dry evacuated Pyrex glass double-limb reaction vessel was loaded with europium metal (0.5 mmol) in the glove box, followed by the addition via vacuum distillation of acetonitrile (5 cm^3) and tungsten hexafluoride (15 mmol). The mixture was allowed to warm up slowly to room temperature, and was shaken for three days. The colour of the solution mixture became pale yellow and a small quantity of a pale yellow solid compound was isolated. The yield of this reaction was very small normally ca. 10mg solid compound was obtained each time. The compound was sensitive to moisture.

On the basis of the infrared spectrum and elemental analysis for the C, H, N and Eu(Table 3.1 and 3.2), the solid was consistent with a mixture of $[Eu(NCMe)_3][WF_6]_3$ and $[Eu(NCMe)_3][WF_7]_3$. The magnetic moment of the solid obtained was determined to be 5.28BM at 298K (Table 3.3). Electronic spectrum of the solid showed a strong band at 29,200 cm^{-1}.

CHAPTER FOUR

REACTIONS BETWEEN THE LANTHANIDE METALS (La, Nd, Eu and Tm) AND THE NITROSONIUM COMPOUNDS, $NOUF_6$, $NOMoF_6$, $NOPF_6$, $NOBF_4$ and $NOWF_7$ IN MeCN

4:1 Introduction

A number of reactions between transition metals and nitrosonium (NO^+) compounds in acetonitrile have been reported in previous work. Some of them are described below.

Oxidation of cobalt, manganese, copper and zinc by $NOClO_4$ in MeCN has been studied.[138] The metals reacted with suspension of $NOClO_4$ in MeCN according to the equation (4-1).

$$M(s) + 2NOClO_4(s) \xrightarrow{MeCN} M^{2+}(solv.) + 2ClO_4^-(solv.) + 2NO(g)$$

$$\longrightarrow [M(NCMe)_x][ClO_4]_2(s) \qquad (4\text{-}1)$$

x=4 for M=Mn, Cu, Zn, and x=6 for M=Co.

Hathaway et al. have investigated the reactions between the transition metals, manganese, iron, cobalt, nickel, copper, zinc and $NOBF_4$ in MeCN. From these reactions, bivalent transition metal tetrafluoroborate-acetonitrile complexes have been prepared.[78] The reactions of these metals with suspensions of $NOBF_4$ in MeCN are described on the basis of equation (4-2).

$$M(s) + 2NOBF_4(s) \xrightarrow{MeCN} M^{2+}(solv.) + 2BF_4^-(solv.) + 2NO(g)$$

$$\longrightarrow [M(NCMe)_x][BF_4]_2(s) \qquad (4\text{-}2)$$

x=4 for M=Zn, Cu, Mn, and x=6 for M=Fe, Co, Ni.

All of the above solvated metal cations that were obtained were in the +2 oxidation state except for copper, where a mixture of Cu(I) and Cu(II) species was formed.

Iqbal[136] studied the reactions between silver, or gold and $NOPF_6$, or $NOMoF_6$ in acetonitrile. He found that the oxidation of gold metal by $NOPF_6$ or $NOMoF_6$ in MeCN was more difficult than that of silver metal. Reactions involving gold were slow, requiring 12 hours for completion and the product yields were also small. Prouff[113] has investigated the oxidation of cobalt, nickel and zinc by $NOPF_6$ in acetonitrile and some complexes containing coordinated acetonitrile were produced. Siddique[135] prepared the complexes, $TlMoF_6$ and $TlUF_6$ by the reactions between thallium and $NOMoF_6$, or $NOUF_6$ in acetonitrile. No coordinated acetonitrile was found in the compounds. All reactions above are described in equation (4-3).

$$N(s) + NOMF_6(s) \xrightarrow{MeCN} N^{n+}(solv.) + MF_6^-(solv.) + NO(g)$$

$$\longrightarrow [N(NCMe)_x][MF_6]_n(s) \qquad (4\text{-}3)$$

x=2, n=1, M=P, or Mo for N=Ag, Au; x=6, n=2, M=P for N=Co, Ni, Zn; and x=0, M=Mo, or U for N=Tl.

Thomas et al. studied the reaction[79] between europium metal and suspension of $NOBF_4$ in MeCN. A orange compound was synthesized according to the reaction(4-4). The stoichiometry of the isolated product corresponded to $[Eu(NCMe)_3(BF_4)_3]$. It was

also found from a molecular weight measurement that the compound was a dimer in MeCN solution.

$$Eu(s) + 3NOBF_4(s) \xrightarrow{MeCN} [Eu(NCMe)_3(BF_4)_3]_2 + 3NO(g) \quad (4\text{-}4)$$

The oxidizing ability of the NO^+ cation has been investigated by cyclic voltammetry. In comparison with the hexafluorides of uranium, molybdenum and tungsten, the following sequence[77] was obtained:

$$\mathbf{UF_6 > MoF_6 > NO^+ > WF_6}$$

The NO^+ cation in MeCN is regarded as a stronger oxidizing agent than tungsten hexafluoride. To date NO^+ salts containing different anions are considered to behave identically since anion and cation are considered to be well separated in solution. However, some differences in behaviour among different NO^+ salts were found in the present work. Some NO^+ compounds, such as $NOUF_6$ did not react with any of the lanthanide metals used while others did react.

4:2 Results

4:2:1 Investigation of the Reactions of La, Nd, Eu and Tm with $NOWF_7$ or $NOUF_6$, La, Nd, Tm with $NOBF_4$, and La, Eu, Tm with $NOMoF_6$ in MeCN

The reactions between La, Nd, Eu, Tm and $NOWF_7$ or $NOUF_6$, La, Nd, Tm and $NOBF_4$, La, Eu, Tm and $NOMoF_6$ in acetonitrile

have been attempted, but were unsuccessful. In all cases there was no evidence of any reaction occurring.

4:2:2 Oxidation of Eu by $NOBF_4$, Nd by $NOMoF_6$ and La, Nd, Eu, Tm by $NOPF_6$ in MeCN

The reaction between europium metal and nitrosonium tetrafluoroborate in acetonitrile at room temperature has been reported in the literature[79]. The reaction was also carried out in the present work and an orange solid was obtained. The infrared spectrum of the solid indicated that it contained coordinated MeCN, the spectrum also showed the presence of the anion BF_4^- (Table 4.1). Two bands at 2310 cm^{-1} and 2280 cm^{-1} were, respectively, assigned to a combination of vibrational modes of CH_3CN ($\upsilon_3+\upsilon_4$) and the C≡N stretch (υ_2). The bands at 1100-1000 and 520 cm^{-1} were assigned to the υ_3 and υ_4 vibrational modes of BF_4^-, respectively. According to the previous work, the stoichiometry of the solid is $[Eu(NCMe)_3(BF_4)_3]$. It has been proposed[79] that this compound contains bridging BF_4^- ions.

The oxidation of neodymium metal by nitrosonium hexafluoromolybdate in MeCN at room temperature resulted in the formation of two different solids. If the reaction time was limited to one day, a yellow solid was isolated from the resulting reaction solution. If the reaction was prolonged, the yellow reaction solution became gradually green and after five days, a green solid was isolated. The infrared spectra of the two solids were almost identical, no significant difference was found. Both

Table 4.1

Infrared spectrum (cm^{-1}) of $[Eu(NCMe)_3(BF_4)_3]_x$

This work	Literature[79]	Assignment
2310(s)	2310(s)	Comb.$CH_3CN(\upsilon_3+\upsilon_4)(A_1)$
2280(s)	2280(s)	C≡N Str. (υ_2) (A_1)
1100-1000(s. b.)	1200-1000(s. b.)	BF_4^- (υ_3)
520(m)	———	BF_4^- (υ_4)

s: strong; s. b. : strong and broad; m: medium; w: weak.

of them showed the coordination of acetonitrile and also indicated the presence of the anion MoF_6^- (Table 4.2). A band attributed to MoF_6^- (υ_3) was observed at 630 cm^{-1} for the yellow solid and at 650 cm^{-1} for the green solid. A band at 250 cm^{-1} in both cases was assigned to MoF_6^- (υ_4). The presence of two bands at 2330 and 2295 cm^{-1} in the two solids was evidence for coordination of acetonitrile and the former was attributed to a combination of vibrational modes of CH_3CN ($\upsilon_3+\upsilon_4$), the latter was assigned to the vibrational mode of C≡N stretch (υ_2). The bands at 1020 and 945 cm^{-1} for the yellow solid, and 1030 and 950 cm^{-1} for the green solid were assigned to the CH_3 rock (υ_7) and C-C stretch (υ_4), respectively.

The course of the reaction was followed by electronic spectroscopy. A band at 630nm which was not observed in the yellow solution was found in the pale green solution obtained after two days of the reaction, and it became more intense with time. It was not regarded as a f-f transition because this would be Laporte forbidden and hence very weak, and it is also believed that it was not a 4f-5d transition due to this kind of transition normally appearing in the ultra-violet region.

The stoichiometry of the solids obtained here should be identical with the compound $[Nd(NCMe)_3][MoF_6]_3$ generated from the reaction between Nd metal and MoF_6 in acetonitrile. However, the microanalysis (Table 4.3) of the yellow solid for the carbon, hydrogen and nitrogen indicated that the quantities

Table 4.2

Infrared Spectra (cm^{-1}) of the Solids from the Reaction between Nd and $NOMoF_6$

Yellow Solid	Green Solid	Assignment
2330(s)	2330(s)	Comb.$CH_3CN(\upsilon_3+\upsilon_4)(A_1)$
2295(s)	2295(s)	C≡N Str. (υ_a) (A_1)
1020(s)	1030(s)	CH_3 Rock (υ_7) (E)
945 (w)	950 (w)	C-C Str. (υ_4) (A_1)
630 (s)	650 (s)	MoF_6^- (υ_3)
250 (s)	250(s)	MoF_6^- (υ_4)

s: strong; m: medium; w: weak.

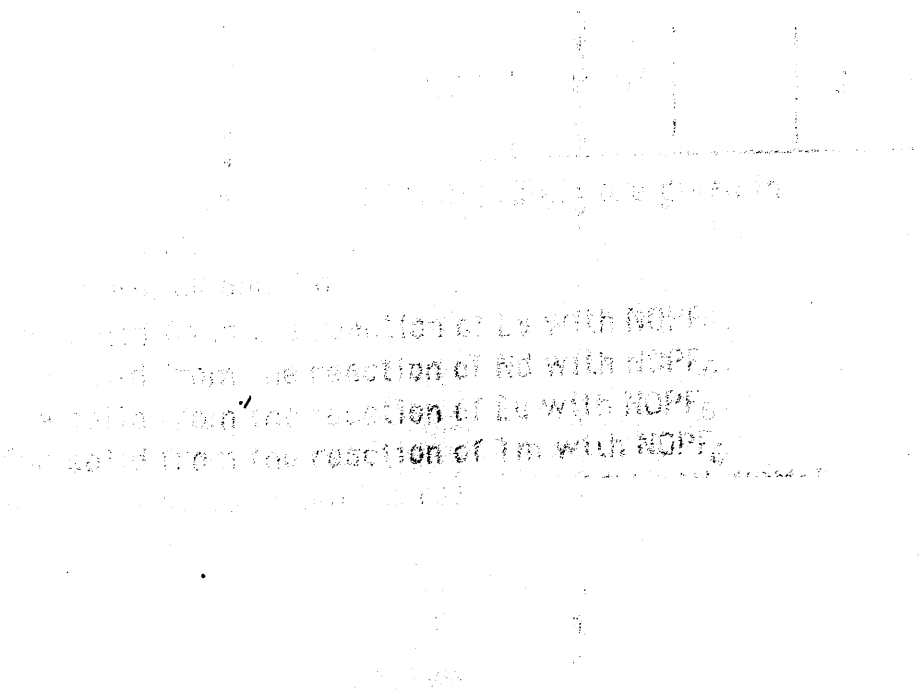


Table 4.3

Analytical data[a] for the solids from the reactions of the lanthanides with $NOMF_6$ (M=P, Mo)

Solid	Colour	Analysis(%)				Atomic ratio
		C	H	N	Ln[b]	C : H : N : Eu
A	Pale yellow	-	-	-	8.17 (19.93)	——
B	Pale yellow	-	-	-	6.25 (20.54)	——
C	Pale yellow	3.75 (10.16)	0.35 (1.28)	3.31 (5.93)	7.25 (21.43)	6.5 : 7.3 : 5 : 1 (6 : 9 : 3 : 1)
D	Pale yellow	3.81 (9.92)	0.45 (1.25)	4.12 (5.79)	8.72 (23.26)	6.2 : 8.7 : 5.7:1 (6 : 9 : 3 : 1)
E	yellow	5.41 (8.03)	0.49 (1.01)	7.01 (4.09)	-	2 : 2.2 : 2 (2 : 3 : 1)
F	green	16.95	3.77	7.55	-	2.6 : 6.9 : 1

a: Required values in $[Ln(NCMe)_3][MF_6]_3$ are given in parentheses.

b: Ln=La, Nd, Eu and Tm.

A: The solid from the reaction of La with $NOPF_6$.

B: The solid from the reaction of Nd with $NOPF_6$.

C: The solid from the reaction of Eu with $NOPF_6$.

D: The solid from the reaction of Tm with $NOPF_6$.

E and F: The solids from the reaction of Nd with $NOMoF_6$.

of the carbon and hydrogen were smaller than those required in $[Nd(NCMe)_3][MoF_6]_3$ and the quantity of the nitrogen was higher than that required. The atomic ratio (Table 4.3) of the C, H and N was 2:2.2:2 (the required atomic ratio is 2:3:1). The results are consistent with the reaction being incomplete in the yellow case and the yellow solid obtained was probably a mixture of $[Nd(NCMe)_3][MoF_6]_3$ and unreacted $NOMoF_6$. For the green solid, the microanalysis(Table 4.3) for the C, H and N indicated that the quantities of the three elements were higher than those required in the compound $[Nd(NCMe)_3][MoF_6]_3$. The atomic ratio (Table 4.3) of the C, H and N was 2.6:6.9:1. No formula was found to correspond to the green solid, from the present work, it was difficult to understand what happened.

Oxidation of La, Nd, Eu and Tm metals by nitrosonium hexafluorophosphate in acetonitrile resulted in the formation of four pale yellow solids, **A, B, C, D**. If the reactions were performed for long times, a slow polymerization of solvent occurred, which was probably caused by the Lewis acid Ln(III) generated during the course of the reaction.

Compared with the compounds $[Ln(NCMe)_3][MF_6]_3$ (Ln=La, Nd, or Eu; M=Mo or W), as described in chapter three, the lanthanides in the solids obtained here should also be in the +3 oxidation state and they should also have three coordinated acetonitrile molecules. The stoichiometries of the solids should be identical with the formulation $[Ln(NCMe)_3][PF_6]_3$. However, the microanalysis of the C, H and N for the solids **C** and **D** (Table 4.3) revealed that the quantities of these elements in the solids were far less than those required in the $[Ln(NCMe)_3][PF_6]_3$, less

even than those required in the $[Ln(NCMe)][PF_6]_3$. The quantities of the lanthanide metals in the four solids were determined from EDTA titrations. The values were also far away from those required for the above stoichiometries. The atomic ratio (Table 4.3) of the C, H, N and Ln in the solids **C** and **D** also showed that the quantity of the N was higher than that required, which was possibly due to the N from the unreacted NO^+ salt. The data indicated that the solids were probably mixtures of $[Ln(NCMe)][PF_6]_3$ and unreacted $NOPF_6$. Hence the reactions did not go to completion.

Although the reactions were incomplete, they did occur. The infrared spectra of the four solids were almost identical and all showed the coordination of acetonitrile and the presence of the anion PF_6^- (Table 4.4). The bands at 840, 740 and 560 cm^{-1} were assigned to the υ_3, υ_1 and υ_4 vibrational modes of PF_6^-, respectively. Two bands at ca. 2330 and 2310 cm^{-1} were attributed to a combination of vibrational modes of CH_3CN ($\upsilon_3+\upsilon_4$) and the bands at ca. 2280 and 1030 cm^{-1} were assigned to the C≡N stretch (υ_2) and CH_3 rock (υ_7), respectively. A band at ca. 940 cm^{-1} was assigned to the C-C stretch (υ_4). The vibrational mode of PF_6^- (υ_1) in the solids is infrared inactive, but it appeared in the infrared spectra, suggesting that there was a distortion of the O_h symmetry of the anion PF_6^-. A possible reason for this is the existence of some interactions between the cations and the anion PF_6^-.

The electronic spectra of the solids formed all produced a strong band in the ultra-violet region, the extinction coefficients

Table 4.4

Infrared Spectra (cm^{-1}) of the Solids from

the reactions of Ln metals with $NOPF_6$

A	B	C	D	Assignment
2340(m)	2330(m)	2340(s)	2330(s)	Comb.CH_3 CN($\upsilon_3+\upsilon_4$)(A_1)
2310(s)	2310(s)	2310(s)	2310(m)	
2280(s)	2280(s)	2285(s)	2290(s)	C≡N Str. (υ_2) (A_1)
1040(w)	1030(w)	1020(w)	1020(w)	CH Rock (υ_7) (E)
	940(w)	940(w)		C-C Str. (υ_4) (A_1)
840(s)	840(s)	840(s)	840(s)	PF_6^- (υ_3)
740(m)	740(m)	740(m)	740(m)	PF_6^- (υ_1)
560(s)	560(s)	560(s)	560(s)	PF_6^- (υ_4)

A=$[La(NCMe)_3][PF_6]_3$; B=$[Nd(NCMe)_3][PF_6]_3$;

C=$[Eu(NCMe)_3][PF_6]_3$; D=$[Tm(NCMe)_3][PF_6]_3$.

s: strong; m: medium; w: weak.

Table 4.5

Electronic Spectrum of $[Ln(NCMe)_3][PF_6]_3$ in MeCN

Complex	$\nu_{max(cm^{-1})}$	Assignment
$[La(NCMe)_3][PF_6]_3$	26,300 (ε =85)	C. T.
$[Nd(NCMe)_3][PF_6]_3$	33,000 (ε =90)	4f-5d or C. T.
$[Eu(NCMe)_3][PF_6]_3$	26,400 (ε =81)	4f-5d or C. T.
$[Tm(NCMe)_3][PF_6]_3$	34,500 (ε =92)	4f-5d or C. T.

C. T. __ charge transfer.

were calculated from the percentages of the lanthanide elements determined in the solids and are given in Table 4.5. The band for the solid **A** was attributed to a charge transfer band and the other bands for the solids **B, C** and **D** were considered to be either the charge transfer or the allowed 4f-5d transition. A shift to lower energy was found in all cases by a comparison with the the electronic spectra of the compounds $[Ln(NCMe)_3][MF_x]_3$ (Ln=La, Nd and Eu; M=Mo and W; x=6 or 7) described in chapter three. It appears that the positions of the bands are sensitive to the anion present.

4:3 Conclusion

The reactions occurring between the lanthanide metals (La, Nd, Eu and Tm) and the NO^+ salts used in acetonitrile at room temperature are given below.

Table 4.6
Survey of the Reactions Occurring between the Lanthanide Metals and the NO^+ Salts

	La	Nd	Eu	Tm
$NOUF_6$	no	no	no	no
$NOWF_7$	no	no	no	no
$NOBF_4$	no	no	re.	no
$NOMoF_6$	no	re.	no	no
$NOPF_6$	re.	re.	re.	re.

re.-reaction; no-no reaction.

4:4 Experimental

Lanthanum metal powder, purity 99.9% (Johnson Matthey Company); neodymium metal powder, or ingot, purity 99.9% (Johnson Matthey Company); europium metal powder, purity 99.9% (Cambrian Chemicals Ltd.); thulium metal powder, purity 99.9% (Halewood Chemicals Ltd.) were used as supplied and stored in the glove box. Nitrosonium hexafluorophosphate, $NOPF_6$ (Fluorochem Ltd.) was used as supplied and stored in the glove box. Nitrosonium tetrafluoroborate, nitrosonium heptafluorotungstate, nitrosonium hexafluoromolybdate and nitrosonium hexafluorouranate were prepared according to the methods described in chapter two and stored in sealed Pyrex glass ampoules at low temperature. Acetonitrile (Rathburn Chemicals Ltd.), HPLC grade, was purified according to the method described in chapter two and stored over activated 3A molecular sieves. Weighing of the chemicals inside the glove box was accomplished by means of an electronic balance (Sartorius Model 1205 MP) with an estimated error of $\pm$ 0.004 g.

4:4:1 Investigation of Reactions between La, Nd, Eu and Tm Metals and $NOWF_7$ in MeCN

A previously evacuated and flamed out double-limb reaction vessel was loaded with one of the lanthanide metals used (0.5 mmol) and nitrosonium heptafluorotungstate (1 mmol) in the glove box. Acetonitrile (5 cm^3) was added to the double-limb reaction vessel by vacuum distillation. The reaction mixture was

allowed to warm up slowly to room temperature and shaken for three days. The suspension of $NOWF_7$ did not change in colour. A colourless solid was isolated when the volatile solvent and unreacted lanthanide metals were removed. As identified by the infrared spectrum it was found to be $NOWF_7$.

4:4:2 Investigation of Reactions between La, Nd, Eu and Tm Metals and $NOUF_6$ in MeCN

One of the lanthanide metals (La, Nd, Eu or Tm) (0.5 mmol) and $NOUF_6$ (1 mmol) were added into a dry evacuated double-limb reaction vessel in the glove box. Acetonitrile (5 cm^3) was added into the reaction vessel by vacuum distillation. The reaction mixture was allowed to warm up to room temperature and then shaken for three days. No colour change of the suspension was observed and no evolution of gas was observed. The solution phase was decanted into another limb for separating the unreacted lanthanum metal and after removal of the volatile solvent, a pale green solid was isolated. It was $NOUF_6$ as identified by its infrared spectrum.

4:4:3 Investigation of Reactions between La, Nd and Tm Metals and $NOBF_4$ in MeCN

A dry evacuated double-limb reaction vessel was loaded with one of the lanthanide metals (La, Nd or Tm) (0.5 mmol) and $NOBF_4$ (1 mmol) in the glove box. Acetonitrile (5 cm^3) was distilled into the reaction vessel. The mixture was allowed to warm up to room temperature and shaken for three days. No

colour change in the suspension was observed and a colourless solid was isolated after separating the unreacted lanthanide metal and removing the volatile solvent. The solid was identified as $NOBF_4$ by its infrared spectrum.

4:4:4 Investigation of Reactions of La, Eu and Tm Metals and $NOMoF_6$ in MeCN

A dry evacuated double limb reaction flask was loaded with one of the lanthanide metals (0.5 mmol) and $NOMoF_6$ (1 mmol) in the glove box. Acetonitrile (5 cm^3) was distilled into the reaction vessel. The mixture was allowed to warm up to room temperature and shaken for three days. No colour change in the mixture was observed and a orange solid was isolated after separating the unreacted lanthanide metal and removing the volatile solvent. The orange solid was identified as $NOMoF_6$ by its infrared spectrum.

4:4:5 Reaction of Europium Metal with Nitrosonium Tetrafluoroborate in Acetonitrile

A previously evacuated and flamed out double-limb reaction vessel was loaded with europium metal (1mmol) and $NOBF_4$ (0.5 mmol) in the glove box. Acetonitrile (5 cm^3) was added to the reaction vessel by vacuum distillation. The mixture was allowed to warm up slowly to room temperature and gas was evolved, presumed to be NO. The reaction mixture was shaken for a day, the NO gas generated in the course of the reaction was removed

periodically by freezing the solution mixture and pumping it under vacuum. The solution mixture became orange in colour finally, and an orange solid was obtained from the resulting solution after removal of unreacted europium metal and volatile solvent. The infrared spectrum (Table 4.1) of the solid indicated the coordination of acetonitrile and the presence of the anion BF_4^-. According to the literature[79], the stoichiometry of the orange solid prepared is $[Eu(NCMe)_3(BF_4)_3]$.

4:4:6 Reaction of Neodymium Metal with Nitrosonium Hexafluoromolybdate in Acetonitrile

Neodymium metal (1 mmol) and $NOMoF_6$ (0.5 mmol) were added into a previously evacuated and flamed out double-limb reaction vessel in the glove box. Acetonitrile (5 cm^3) was distilled into the double-limb reaction vessel at low temperature. When the reaction mixture reached room temperature, bubbles of gas were evolved from the mixture, which were presumed to be NO. The mixture was shaken for a day and NO gas generated was removed periodically from the reaction vessel. The solution changed to yellow from the original orange colour due to the $NOMoF_6$. A yellow solid was isolated after removing the unreacted neodymium metal and the volatile solvent. If the mixture was shaken for a longer time, it became gradually green until after five days the mixture was deep green. After the volatile material was removed, a deep green solid was isolated. Although the infrared spectra of both solids (Table 4.2) showed the coordination of acetonitrile and the presence of the anion

MoF_6^-, the microanalysis (Table 4.3) for the C, H and N indicated that the atomic ratio of the C, H and N was 2:2.2:2 for the yellow solid and 2.6:6.9:1 for the green solid. The atomic ratio for the yellow solid showed that the quantity of the N was higher than that required due to the N from the unreacted NO^+ salt, that is, the reaction did not go to completion to produce the yellow solid. However, no satisfactory formulation was found for the green solid. The course of the reaction was also followed by electronic spectroscopy. A band at 630 nm was found only in the pale green solution formed after two days of the reaction, becoming very strong after five days of the reaction.

4:4:7 Oxidation of La, Nd, Eu and Tm Metals by Nitrosonium Hexafluorophosphate in MeCN

A dry evacuated double-limb reaction flask was loaded with one of the lanthanum metals (1 mmol) and $NOPF_6$ (0.5 mmol) in the glove box. Acetonitrile (5 cm^3) was distilled into the reaction vessel at low temperature. When the mixture reached room temperature, bubbles were evolved from the mixture, they were assumed to be NO gas and removed periodically during the course of the reaction. When the mixture was shaken for a day, the solution mixture became pale yellow, and a pale yellow solid was isolated after removal of the volatile material and unreacted metal. If the mixture was shaken for a longer time, the evolution of gas was again observed from the mixture. However, the colour of the solution mixture became brown, and finally the mixture was sticky brown presumably due to the polymerization of solvent. Although the infrared spectra (Table 4.4) of the pale

yellow solids showed the presence of coordinated acetonitrile and the anion PF_6^-, the elemental analysis (Table 4.3) of the solids indicated that the quantities of the N in the atomic ratio of the C, H, N and Ln for the solids **C** and **D** were higher than those required, and the quantities of the Ln in all solids were smaller than those required. Therefore, they were possibly mixtures of $[Ln(NCMe)_3][PF_6]_3$ and unreacted $NOPF_6$, and hence the reactions were incomplete.

CHAPTER FIVE

REACTIONS OF PYRIDINE (py) AND TRIMETHYLAMINE (Me_3N) WITH $[Ln(NCMe_3)][MF_6]_3$ (Ln=La, Nd, or Eu; M=Mo or W; x=6 or 7) OR $NOPF_6$ IN MeCN

5:1 Introduction

Two ligands were used to displace the coordinated acetonitrile in the compounds prepared in this work; they were the simple N-donor species, trimethylamine and pyridine. These are regarded as comparatively weak ligands compared with chelating and macrocyclic ligands which possess greater stabilizing ability. The main objective in selecting NMe_3 and pyridine as ligands in the present work was to investigate whether a weak N-donor ligand can displace acetonitrile at solvated lanthanide cations in acetonitrile. In previous work,[135] the coordinated acetonitrile in the hexakis(acetonitrile) iron(II) cation was displaced by py or NMe_3 at room temperature in the presence or absence of acetonitrile. An off-white solid isolated from the reaction of $[Fe(MeCN)_6][PF_6]_2$ with neat pyridine was identified as $[Fe(py)_6][PF_6]_2$ on the basis of its infrared spectrum and elemental analysis. However, the compound obtained from the reaction of $[Fe(MeCN)_6][PF_6]_2$ with pyridine in acetonitrile was analytically and spectroscopically identical to the product isolated from the dissolution of $[Fe(py)_6]\{PF_6]_2$ in acetonitrile, that is, $[Fe(py)_5(MeCN)][PF_6]_2$. An off-white solid obtained from the reaction of $[Fe(MeCN)_6][PF_6]_2$ with trimethylamine in the absence or presence of acetonitrile was characterized as $[Fe(NMe_3)(MeCN)_4][PF_6]_2$ on the basis of its infrared spectrum and microanalysis. Here, the apparent coordination number of the Fe(II) ion is only five which is in contrast to the normal situation for the Fe(II) ion whose coordination number is usually six. A possible explanation is that

loss of one acetonitrile ligand occurs during the isolation of the compound since MeCN is weakly bound to metal cations. On the basis of the ligand field strengths of the py, NMe_3 and MeCN towards iron(II), the order of these simple nitrogen donor ligands appears to be

$$\mathbf{py > NMe_3 > MeCN}$$

5:2 Results

5:2:1 Preparation of $[Ln(py)_7(NCMe)][MF_x]_3$ from the Reactions of $[Ln(NCMe)_3][MF_x]_3$ with py in MeCN (Ln=La, Nd or Eu; M=Mo or W; x=6 or 7)

The reactions of the solid compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6, or 7) described in chapter three with pyridine in acetonitrile resulted in the formation of four solid compounds **A, B, C, D**. They were almost insoluble in acetonitrile. The infrared spectra of the complex compounds indicated that they contained both coordinated pyridine and acetonitrile, the spectra also showed the presence of the anions MoF_6^- or WF_6^- and WF_7^-. Bands were assigned by comparison with the infrared spectra of free pyridine and acetonitrile,[139,140] the assignments made are given in Table 5.1. Microanalysis for carbon, hydrogen and nitrogen in the solid complexes indicated that the stoichiometries of the solids **B, C** were consistent with the formulation $[Ln(py)_7(NCMe)][MoF_6]_3$ (Ln=Nd, or Eu) and the stoichiometries of the solids **A, D** were consistent with either the

Table 5.1

Infrared Spectra (cm^{-1}) of the Solid Salts

A=$[La(Py)_7(MeCN)][WF_x]_3$; B=$[Nd(Py)_7(MeCN)][MoF_6]_3$;
C=$[Eu(Py)_7(MeCN)][MoF_6]_3$; D=$[Eu(Py)_7(MeCN)][WF_x]_3$. x=6, or 7.

A	B	C	D	Assignment	Corresponding bonds of the free ligands 139,140
2330(w)	2330(w)	2330(w)	2330(w)	Comb. CH_3CN ($\upsilon_3+\upsilon_4$)(A_1)	2293
2295(w)	2295(w)	2295(w)	2295(w)	C≡N Str. (υ_3)(A_1)	2254
1640(w)	1635(w)	1640(w)	1640(w)	Coord. py	1627
1606(m)	1610(s)	1606(s)	1607(m)	Coord. py	1578
1565(w)	1540(m)	1540(m)	1540(m)	Coord. py	1570
1483(m)	1480(s)	1490(s)	1490(m)	Coord. py	1478
1448(s)	1448(s)	1448(s)	1445(m)	Coord. py	1436
1215(w)	1210(m)	1206(w)	1255(w)	Coord. py	1217
	1170(w)	1170(w)	1170(w)	Coord. py	1145
1070(w)	1064(s)	1065(m)	1070(w)	Coord. py	1067
	1047(m)			Coord. py	1031
	1015(m)	1018(w)		Coord. py	991
970(m)	950(s)	950(m)	970(m)	Coord. py	942
765(w)	850(m)	760(m)	753(m)	Coord. py	747
725(w)	712(s)		725(w)	Coord. py	700
	690(s)	690(m)		Coord. py	650
690(w)			680(w)	Coord.py+WF_7^-	
	630(s)	625(m)		MoF_6^- (υ_3)	
600(m)			615(s)	WF_6^- (υ_3)	
	260(m)	260(m)		MoF_6^- (υ_4)	

s: strong; m: medium; w: weak.

formulation $[Ln(py)_7(NCMe)][WF_6]_3$ (Ln=La, or Eu) or the formulation $[Ln(py)_7(NCMe)][WF_7]_3$ (Ln=La, or Eu) (Table 5.2). Therefore, **A** and **D** were regarded as a mixture of $[Ln(py)_7(NCMe)][WF_6]_3$ and $[Ln(py)_7(NCMe)][WF_7]_3$ (Ln=La, or Eu). The atomic ratios found in the complexes and those required in the complexes are given in Table 5.3, and compared with ratios required by other formulations. Tables 5.2 and 5.3 indicate that the stoichiometries suggested above for the complexes are the most probable. The apparent coordination number of the cation was eight in each case, which is consistent with the normal situation for lanthanide complexes. It appears that pyridine is a stronger ligand than acetonitrile, but precipitation of the complexes makes a proper comparison ambiguous.

5:2:2 Preparation of $[Ln(NMe_3)_4(NCMe)_2][MF_x]_3$ from the Reactions of $[Ln(NCMe)_3][MF_x]_3$ with Trimethylamine in MeCN (Ln=La, Nd, or Eu; M=Mo, or W; x=6, or 7)

The four solid complexes, **E, F, G** and **H**, were formed very quickly from the reactions of NMe_3 with the compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6, or 7) in acetonitrile. They were almost insoluble in acetonitrile. The infrared spectra of the solid complexes formed indicated the coordination of acetonitrile and trimethylamine by the bands at about 2330, 2295 cm^{-1} for acetonitrile and the bands at about 3030 and 1480 cm^{-1} for

Table 5.2

Analytical data[a] for lanthanide(III) complexes

Complex	Colour	Analysis (%)		
		C	H	N
$[La(py)_7(MeCN)][WF_6]_3$ or $[La(py)_7(MeCN)][WF_7]_3$	dark brown	26.90 (27.31) [26.38]	1.98 (2.35) [2.27]	6.68 (6.89) [6.66]
$[Nd(py)_7(MeCN)][MoF_6]_3$	pink	32.79 (32.46)	2.71 (2.80)	7.81 (8.09)
$[Eu(py)_7(MeCN)][MoF_6]_3$	deep yellow	32.10 (32.28)	2.76 (2.78)	7.90 (8.10)
$[Eu(py)_7(MeCN)][WF_6]_3$ or $[Eu(py)_7(MeCN)][WF_7]_3$	brown	26.60 (27.09) [26.18]	2.60 (2.34) [2.26]	6.50 (6.80) [6.60]
$[La(NMe_3)_4(MeCN)_2][WF_6]_3$ or $[La(NMe_3)_4(MeCN)_2][WF_7]_3$	dark brown	14.20 (14.22) [13.65]	3.58 (3.13) [3.01]	6.30 (6.22) [5.97]
$[Nd(NMe_3)_4(MeCN)_2][MoF_6]_3$	pink	17.30 (17.59)	3.27 (3.88)	7.63 (7.70)
$[Eu(NMe_3)_4(MeCN)_2][MoF_6]_3$	deep yellow	17.52 (17.48)	3.79 (3.85)	7.69 (7.64)
$[Eu(NMe_3)_4(MeCN)_2][WF_6]_3$ or $[Eu(NMe_3)_4(MeCN)_2][WF_7]_3$	brown	14.25 (14.10) [13.52]	3.30 (3.10) [2.98]	6.37 (6.20) [5.92]

[a] : Required values are given in parentheses for MF_6^- salts (M=Mo,or W) and in square brackets for WF_7^- salts.

Table 5.3

Atomic ratios found in the Ln(III)-py complexes

Complex	C	H	N
A	37.6	33.0	8.0
B	39.2	38.6	8.0
C	37.9	38.9	8.0
D	38.2	44.5	8.0

Atomic ratios required in the Ln(III)-py complexes with different formulations

Complex	C	H	N
$[Ln(py)_7(MeCN)][MF_x]_3$	37	38	8
$[Ln(py)_7(MeCN)_2][MF_x]_3$	39	41	9
$[Ln(py)_6(MeCN)_2][MF_x]_3$	34	36	8
$[Ln(py)_6(MeCN)_3][MF_x]_3$	36	39	9
$[Ln(py)_8(MeCN)][MF_x]_3$	42	43	9

Ln=La, Nd or Eu; M=Mo or W; x=6 or 7.

trimethylamine, and also showed the presence of the anions MoF_6^- or WF_6^- and WF_7^-. Bands were assigned by comparison with the infrared spectra of free trimethylamine and acetonitrile,[140,141] some assignments made are given in Table5.4. On the basis of the microanalysis (Table 5.2) of the carbon, hydrogen and nitrogen for the complexes prepared, the stoichiometries of the solid complexes **F** and **G** were consistent with the formulation $[Ln(NMe_3)_4(NCMe)_2][MoF_6]_3$(Ln=Nd, or Eu) and the stoichiometries of the solids **E** and **H** were consistent with either $[Ln(NMe_3)_4(NCMe)_2][WF_6]_3$ or $[Ln(NMe_3)_4(NCMe)_2][WF_7]_3$ (Ln=La, or Eu), therefore, the solids **E** and **H** were regarded as a mixture of $[Ln(NMe_3)_4(NCMe)_2][WF_6]_3$ and $[Ln(NMe_3)_4(NCMe)_2][WF_7]_3$ (Ln=La, or Eu). A comparison of the atomic ratios found in the complexes with those required for a number of different formulations (Table 5.5) also indicates that the stoichiometries suggested above are the most probable. The apparent coordination number of Ln(III) cation was six in each case. It seems that the trimethylamine is a stronger ligand than acetonitrile, but precipitation of the complexes also makes a proper comparison ambiguous.

5:2:3 Reactions between $NOPF_6$ and py or NMe_3 in MeCN

Because the reactions between py or NMe_3 and the complexes $[Ln(NCMe)_3][MF_x]_3$ (Ln=La, Nd an Eu; M=Mo or W; x=6 or 7) in MeCN all resulted in the formation of the solid complexes which

Table 5.4

Infrared Spectrum(cm^{-1}) of the solid salts

E	F	G	H	Assignment	Corresponding bands of the free ligands 140,141
3050(w)	3030(m)	3023(m)	3040(w)	CH Str. Me_3N	2944
2930(w)	2940(m)	2930(m)	2920(w)	CH Str. MeCN	2878
2330(w)	2330(w)	2330(w)	2330(w)	Comb. MeCN	2293
2295(w)	2295(w)	2295(w)	2295(w)	C≡N Str. MeCN	2254
1480(s)	1480(s)	1480(s)	1480(m)	CH_3Rock Me_3N	1460
1070(w)	1070(m)	1070(w)	1070(w)	CH_3Rock MeCN	1047
980(s)	990(m)	970(w)	980(m)	C-C Str MeCN	917
720(s)			720(m)	WF_7^- ?	
600(s)			600(s)	WF_6^- (υ_3)	
	600(s)	600(m)		MoF_6^- (υ_3)	
	260(s)	260(s)		MoF_6^- (υ_3)	

E=$[La(NMe_3)_4(NCMe)_2][WF_x]_3$; F=$[Nd(NMe_3)_4(NCMe)_2][MoF_6]_3$;

G=$[Eu(NMe_3)_4(NCMe)_2][MoF_6]_3$; H=$[Eu(NMe_3)_4(NCMe)_2][WF_x]_3$.

x=6 or 7; s: strong; m: medium; w: weak.

Table 5.5
Atomic ratios found in the Ln(III)- NMe_3 complexes

Complex	C	H	N
E	15.8	47.4	6.0
F	15.9	35.7	6.0
G	16.0	41.1	6.0
H	15.7	43.2	6.0

Atomic ratios required in the Ln(III)-NMe_3 complexes with different formulations

Complex	C	H	N
$[Ln(NMe_3)_4(MeCN)][MF_x]_3$	14	39	5
$[Ln(NMe_3)_4(MeCN)_2][MF_x]_3$	16	42	6
$[Ln(NMe_3)_4(MeCN)_3][MF_x]_3$	18	45	7
$[Ln(NMe_3)_5(MeCN)][MF_x]_3$	17	48	6
$[Ln(NMe_3)_5(MeCN)_2][MF_x]_3$	19	51	7
$[Ln(NMe_3)_5(MeCN)_3][MF_x]_3$	21	54	8
$[Ln(NMe_3)_3(MeCN)][MF_x]_3$	11	30	4
$[Ln(NMe_3)_3(MeCN)_2][MF_x]_3$	13	33	5
$[Ln(NMe_3)_3(MeCN)_3][MF_x]_3$	15	36	6

Ln=La, Nd or Eu; M=Mo or W; x= 6 or 7.

were almost insoluble in MeCN, it was considered that similar reactions should occur between py or NMe_3 and the impure products obtained from the reactions of La, Nd, Eu and Tm with $NOPF_6$ in MeCN described in chapter four. These reactions should be complete and insoluble products should be easily separated from solvent MeCN and the unreacted $NOPF_6$ which is soluble in MeCN. However, it was necessary to check whether $NOPF_6$ would react with pyridine or trimethylamine. Unfortunately, $NOPF_6$ did react with pyridine or trimethylamine and two solids were obtained.

(1) Preparation of $NOPF_6 \cdot 2py$ by Reaction between py and $NOPF_6$ in Acetonitrile

The reaction between nitrosonium hexafluorophosphate and pyridine in acetonitrile resulted in the formation of a brown solid. The infrared spectrum (Table 5.6) of the solid indicated that it contained coordinated pyridine, the spectrum also showed the presence of the anion PF_6^- and the cation NO^+. Microanalysis (Table 5.7) of the C, H and N and the atomic ratio calculated for the solid indicated that the formulation of the solid was most probably $NOPF_6 \cdot 2py$.

(2) Preparation of $NOPF_6 \cdot 2NMe_3$ by Reaction between $NOPF_6$ and Trimethylamine in Acetonitrile

A pale yellow solid was prepared from the reaction between nitrosonium hexafluorophosphate and trimethylamine in acetonitrile. The infrared spectrum (Table 5.8) of the solid

Table 5.6
Infrared spectrum of the solid $NOPF_6 \cdot 2py$

Wavenumber (cm^{-1})	Assignment	Corresponding bands of the free ligands [139]
2330(w)	NO^+	
1640(w)	Coord. py	1627
1610(m)	Coord. py	1578
1540(m)	Coord. py	1570
1490(w)	Coord. py	1478
1170(w)	Coord. py	1145
1075(w)	Coord. py	1067
975(w)	Coord. py	991
840(s)	PF_6^- (υ_3)	
560(s)	PF_6^- (υ_4)	

s: strong; m: medium; w: weak.

Table 5.7

Analytical data [a] of the solids obtained from the reactions between $NOPF_6$ and py or NMe_3

Solid	C	H	N	Atomic ratio C : H : N
$NOPF_6 \cdot 2py$	36.12 (36.05)	1.52 (3.03)	8.22 (8.41)	5.1 : 2.6 : 1.0 (5 : 5 : 1)
$NOPF_6 \cdot 2NMe_3$	24.20 (24.57)	6.52 (6.20)	9.47 (9.56)	3.0 : 9.6 : 1.0 (3 : 9 : 1)

[a] Required values are given in the parentheses.

Table 5.8

Infrared Spectrum (cm^{-1}) of the Solid $NOPF_6 \cdot 2NMe_3$

Wavenumber	Assignment	Corresponding bands of the free ligand [141]
3250(s)	CH Str.(Me_3N)	2950
2330(w)	NO^+	
1480(s)	CH_3 rock(Me_3N)	1460
1460(s.h)	CH_3 rock	
1075(m)	CN str.	1043
840 (s)	PF_6^- (υ_3)	
560 (s)	PF_6^- (υ_4)	

s: strong; s.h: shoulder; m: medium; w: weak.

showed that it contained coordinated NMe_3, the spectrum also indicated the presence of the cation NO^+ and the anion PF_6^-. Microanalysis (Table 5.7) of the C, H and N and the atomic ratio calculated for the solid indicated that the formulation of the solid was most likely $NOPF_6 \cdot 2NMe_3$.

5:3 Conclusion

Reactions of $[Ln(NCMe)_3][MF_x]_3$ (Ln=La, Nd or Eu; M=Mo or W; x=6 or 7) with py or NMe_3 in acetonitrile resulted in the formation of the following complexes of lanthanides(III).

$[La(py)_7(NCMe)][WF_x]_3$, $[Nd(py)_7(NCMe)][MoF_6]_3$,
$[Eu(py)_7(NCMe)][MoF_6]_3$, $[Eu(py)_7(NCMe)][WF_x]_3$;
x=6, or 7. and
$[La(Me_3N)_4(NCMe)_2][WF_x]_3$, $[Nd(Me_3N)_4(NCMe)_2][MoF_6]_3$,
$[Eu(Me_3N)_4(NCMe)_2][MoF_6]_3$, $[Eu(Me_3N)_4(NCMe)_2][WF_x]_3$.
x=6, or 7.

These complex compounds were all almost insoluble in acetonitrile. According to the coordinating situation of these N-donor ligands in the lanthanide compounds prepared in the present work, py and NMe_3 appeared to be stronger ligands than acetonitrile, however, a proper comparison is difficult due to the precipitation of the complexes.

5:4 Experimental

Trimethylamine (Matheson Ltd.) was purified by repeated distillation over P_2O_5 under vacuum and stored over freshly sublimed P_2O_5 at 77K. Pyridine(BDH, Analar) was distilled from NaOH pellets, collected over 4A molecular sieves, degassed and stored over activated 4A molecular sieves under vacuum. The compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6 or 7) were prepared according to the method described in chapter three. Acetonitrile(Rathburn Chemicals Ltd., HPLC Grade S) was purified according to the method described in chapter two. Weighing of the chemicals inside the glove box was accomplished by means of an electronic balance (Sartorius Model 1205 MP) with an estimated error of $\pm$ 0.004 g.

5:4:1 Reactions of $[Ln(NCMe)_3][MF_6]_3$(Ln=La, Nd or Eu; M= Mo or W; x= 6 or 7) with py in MeCN

A previously flamed out and evacuated double-limb reaction vessel was loaded with one of the compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6, or 7) (10 mg) in the glove box. The reaction vessel was attached to the vacuum line and evacuated. Acetonitrile (5 cm^3) and pyridine (5 cm^3) were in turn distilled into the reaction vessel by vacuum distillation at low temperature. When the solution mixture reached room temperature, an insoluble solid complex was rapidly formed. The

four solids, **A, B, C** and **D**, were obtained from four similar reactions. Their colours are given in Table 5.2. On the basis of their infrared spectra (Table 5.1) and the elemental analysis (Table 5.2), the solids, **A** and **D**, were characterized as a mixture of $[Ln(py)_7(NCMe)][WF_6]_3$ and $[Ln(py)_7(NCMe)][WF_7]_3$ (Ln=La, or Eu) and the solids, **B** and **C**, were characterized as $[Ln(py)_7(NCMe)][MoF_6]_3$ (Ln=Nd, or Eu).

5:4:2 Reactions of $[Ln(NCMe)_3][MF_6]_3$ (Ln=La, Nd, or Eu; M= Mo or W; x= 6 or 7) with NMe_3 in MeCN

One of the compounds $[La(NCMe)_3][WF_x]_3$, $[Nd(NCMe)_3][MoF_6]_3$, $[Eu(NCMe)_3][MoF_6]_3$ and $[Eu(NCMe)_3][WF_x]_3$ (x=6 or 7) (10mg) was added into a dry evacuated double-limb reaction vessel in the glove box, followed by the addition of acetonitrile (5 cm^3) and trimethylamine (0.700g) by vacuum distillation at low temperature. The solution mixture was allowed to warm up slowly to room temperature, and a solid was formed very quickly. The four solid complexes, **E, F, G** and **H**, were obtained from four similar reactions. Their colours are given in Table 5.2. They were almost insoluble in acetonitrile. The solids, **F** and **G**, were identified as $[Ln(NMe_3)_4(NCMe)_2][MoF_6]_3$(Ln=Nd, or Eu) and the solids, **E** and **H**, were identified as a mixture of $[Ln(NMe_3)_4(NCMe)_2][WF_6]_3$ and $[Ln(NMe_3)_4(NCMe)_2][WF_7]_3$ (Ln=Nd, or Eu), on the basis of their elemental analysis (Table 5.2) and infrared spectra (Table5.4).

5:4:3 Reaction between $NOPF_6$ and py in MeCN

A previously evacuated and flamed out double-limb reaction vessel was loaded with $NOPF_6$ (0.5 mmol) in the dry glove box. Acetonitrile (5 cm^3) and pyridine (5 cm^3) were in turn distilled into the reaction vessel at low temperature. The mixture was allowed to warm up to room temperature and it became brown very quickly. After removal of the volatile material, a brown solid was isolated. On the basis of its infrared spectrum (Table 5.6) and microanalysis (Table 5.7) of the C, H and N, the stoichiometry of the solid was regarded as $NOPF_6 \cdot 2py$.

5:4:4 Reaction between $NOPF_6$ and NMe_3 in MeCN

A dry evacuated double-limb reaction vessel was loaded with $NOPF_6$ (0.5 mmol) in the dry glove box. Acetonitrile (5 cm^3) and trimethylamine (0.700g) were in turn distilled into the reaction vessel at low temperature. The mixture was allowed to warm up to room temperature, and it became pale yellow very quickly. After removal of the volatile material, a pale yellow solid was isolated. On the basis of its infrared spectrum (Table 5.8) and the microanalysis (Table 5.7) of the C, H and N, the solid was regarded as $NOPF_6 \cdot 2NMe_3$.

CHAPTER SIX

DISCUSSION

Discussion

The oxidation of lanthanide metals La, Nd, Eu and Tm by MoF_6 and WF_6, as well as by some nitrosonium compounds in acetonitrile has been described in chapters three and four. The reactions between py or NMe_3 and the compounds obtained from the oxidation of the lanthanide metals by MoF_6 and WF_6 have also been described in chapter five. Reactions between the lanthanide metals and the hexafluorides used in acetonitrile produce salts of the solvated lanthanide cations.

$$Ln + 3MF_6 \xrightarrow{MeCN} Ln^{3+}(solv.) + 3MF_6^-(solv.)$$

M=Mo or W for Eu; M=W for La; M=Mo for Nd as pieces of metal ingot freshly cut in the glove box.

The oxidation state of the lanthanides in the compounds obtained from the reactions above is +3, which is reasonable because, except for europium, the metals are found in the +3 oxidation state in most of their compounds. Europium can exist in the +2 and +3 oxidation states in its known compounds, but Eu(II), which is known to be a strong reducing agent in water, is unstable with respect to oxidation and would be unlikely to exist in the environment of the strongly oxidizing hexafluorides used. Europium is oxidized by both MoF_6 and WF_6 in MeCN, but thulium is not oxidized by either hexafluoride. These observations are consistent with expectation on the basis of the reactive sequence of the lanthanide metals Eu > La > Nd > Tm.[2]

Thulium is one of the "heavy earths" of the lanthanides, and it is less reactive than Eu, La and Nd. Europium, which belongs to the "light earths", and has the largest metal radius of all the lanthanide elements, is much the most reactive as was described in chapter one.

Lanthanum is oxidized by WF_6, but not by MoF_6. No reactions between uranium hexafluoride and any of the lanthanide metals have been observed, which is contrary to expectation in view of the reactive sequence of the hexafluorides, $UF_6 > MoF_6 > WF_6$.[77] It is strange that neodymium powder is not oxidized by either MoF_6 or WF_6, but neodymium (as pieces of metal ingot freshly cut in the glove box) is oxidized by MoF_6. The lanthanide metals examined all react with $NOPF_6$, but significant differences among a number of nitrosonium salts containing different anions are found. Some of them do not react with the lanthanide metals in MeCN. These observations are unexpected. The complex compounds isolated in the present work are given in Table 6.1.

As can be seen from Table 6.1, the apparent coordination numbers of the lanthanide cations in the solid state are low and the complexes obtained from the reactions between py or NMe_3 and the compounds $[Ln(NCMe)_3][MF_x]_3$ (Ln=La, Nd or Eu; M=Mo or W; n=6 or 7) are insoluble in MeCN.

The coordination numbers of lanthanide complexes are normally greater than six, as described in chapter one. Apparent coordination numbers are low in some lanthanide complexes

Table 6.1
The complexes obtained in the present work corresponding to each lanthanide metal used

La	Nd	Eu
$[La(NCMe)_3][WF_x]_3$	$[Nd(NCMe)_3][MoF_6]_3$	$[Eu(NCMe)_3][MF_x]_3$
$[La(py)_7(NCMe)][WF_x]_3$	$[Nd(py)_7(NCMe)][MoF_6]_3$	$[Eu(py)_7(NCMe)][MF_x]_3$
$[La(NMe_3)_4(NCMe)_2][WF_x]_3$	$[Nd(NMe_3)_4(NCMe)_2][MoF_6]_3$	$[Eu(NMe_3)_4(NCMe)_2][MF_x]_3$

M=Mo or W; x=6 or 7.

previously described in the literature,[142,143] but the coordination of the anions to the cation both in solution and in the solid state, as demonstrated, results in the actual coordination numbers being large. For example, in the solid compounds[142,143] $Ln(bipy)_2(NO_3)_3$ (Ln=La-Lu; bipy=2,2'- bipyridyl) the apparent coordination numbers are four, due to bipy being a bidentate ligand, but the nitrate frequencies in the infrared spectra of these compounds clearly indicate the absence of ionic nitrate (the strong band at 1380 cm^{-1} corresponding to ionic nitrate is absent) and presence of coordinated nitrate (there are bands at ca. 1500 cm^{-1} and ca. 1300 cm^{-1} corresponding to bidentate coordinated nitrate). Thus the actual coordination numbers are ten. In solution, this kind of interaction between lanthanide(III) cations and the anion is also found. The vibrational spectra of solutions of europium nitrate in acetonitrile show the presence of coordinated MeCN and coordinated nitrate. Nitrate group frequencies, as well as Raman band polarizations are consistent with bidentate (or bridging) anions.[73] Conductimetric measurements indicate that europium nitrate behaves as a nonelectrolyte in acetonitrile, which precludes the presence of uncoordinated (or ionic) nitrate; a weak fluorescence band around 580 nm is assigned to the transition $^5D_0 -> ^7F_0$ of the Eu(III) ion. A maximum of four acetonitrile molecules directly bound to the Eu(III) ion is revealed by the formation of the species $[Eu(NO_3)_5^{2-}]$ when the total concentration of nitrate is increased. The infrared spectrum of this solution is practically identical with the spectrum of the solid pentanitrate, and the crystal structure of such salt demonstrates the presence of five bidentate nitrate groups.[73] Therefore, the Eu(III) cation is

decacoordinated, due to the interaction of the cation and anion. The NO_3^- anion provides a particular example of anion-cation interaction. However, this kind of interaction is not limited to NO_3^-; for example, coordination of $CF_3SO_3^-$ to Ln^{3+} is very common.[144] These observations suggest a hypothesis that there is a interaction between the lanthanide(III) cation and the fluoroanion of the complexes prepared in the present work both in solution and in the solid state.

In many complexes, fluoroanions such as BF_4^-, PF_6^-, MoF_6^- and AsF_6^-, which are very weak bases, are normally considered as non-coordinating with both hard and soft cations[145-148]. However, there are now sufficient examples of interaction between various cations and fluoroanions for such interactions not to be considered unusual. For example, the nature of the cation-anion interaction in the complex, $Ni(4\text{-Mepy})_4(PF_6)_2$ (4-Mepy=4-methylpyridine) has been observed through a single-crystal X-ray diffraction study by Morrison et al.[149] The structure consists of nickel atoms on inversion centres with two pairs of crystallographically different 4-methylpyridine ligands defining a square-planar array around nickel. The hexafluorophosphate groups are crystallographically identical, and are situated above and below the square plane. The PF_6^- anions appear as somewhat distorted octahedra; they are not fully coordinated to nickel, but are nonetheless held in axial positions by weak, essentially ionic, interactions in this complex, as evidenced by the fact that the Ni-F distance is 3.031 Å, which is considerably greater than the covalent bond Ni-F, 1.87 Å.

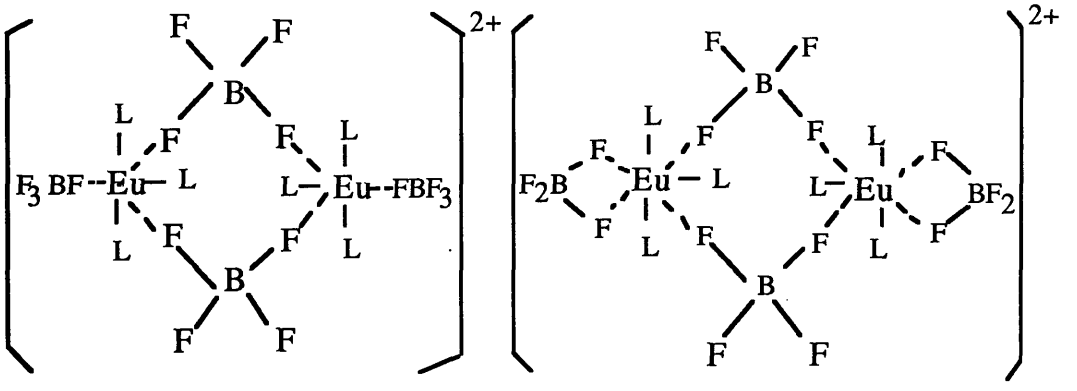
From a combination of electronic, e.p.r. and i.r. spectroscopy, interaction of the PF_6^- anion and the Cu(II) cation has been proposed to be present in the complex, $Cu(py)_4(PF_6)_2$.[150] Similarly, according to the electronic and vibrational spectra and magnetic susceptibility data, it has been suggested that the complex, $Ni(py)_4(AsF_6)_2$, has a structure similar to that of Ni(4-Mepy)$_4$(PF$_6$)$_2$, with the anion weakly interacting with the cation at high temperature and fully coordinated at low temperature.[149]

The interaction of the BF_4^- anion (as a unidentate species) with the cations, Mn(II), Zn(II), Sn(II), has been observed in the complexes,[78] $Mn(NCMe)_4(FBF_3)_2$ and $Zn(NCMe)_4(FBF_3)_2$ by infrared spectroscopy, and in the complex, $SnMe_3(F_2BF_2)$, BF_4^- behaves as a bidentate group.[150] The interaction of the BF_4^- anion with Cu(II) has also been found in the complex, $[CuL_2(FBF_3)_2$,[151] (L=2,5,-dithiohexane) by means of a crystallographic study.

A ^{205}Tl n.m.r. spectroscopy study of the salts $TlUF_6$, $TlPF_6$, $TlMoF_6$ and $TlWF_x$ (x=6 or 7) in acetonitrile solution indicates the presence of definite cation-anion interactions, which results in some degree of ion-pairing in these salts.[135]

Although few examples of interaction between cations and fluoroanions are available for lanthanide complexes, there is one reported example in the complex, $Eu(NCMe)_3(BF_4)_3$. This is obtained from the reaction of Eu metal with $NOBF_4$ in

acetonitrile.[79] Although the infrared spectrum of the solid compound has not provided any information about interaction between Eu(III) and BF_4^-, this compound has been found to be a dimer in acetonitrile solution by a molecular weight measurement of isothermal distillation. This suggests the presence of bridging BF_4^-, and this compound in MeCN exhibits a conductivity of 298 $\Omega^{-1}cm^2mol^{-1}$, a value that falls within the observed range for a 1:2 electrolyte. Two structural possibilities, A and B, for the cation are given below by combining the information which is known. As can been seen from A and B, the Eu(III) cation is six-coordinate in structure A, and seven-coordinate in structure B. Thus this kind of interaction between a lanthanide(III) cation and the fluoroanion can account for the apparent paucity of ligands around the lanthanide(III) cation.



(A) (B)

From this point of view, it is reasonable to assume that there may be some interactions of the cation and the anions MoF_6^- and WF_6^- in the complexes prepared in the present work, which might be responsible for the magnetic moments of the complexes

being low and results in the actual coordination numbers of the lanthanide(III) cation being greater than are apparent in the complexes.

Many lanthanide complexes are soluble in either water or organic solvents; for example, the compounds[152] $LnX_3L \cdot mCH_3CN$ (Ln=La, Pr, Nd, Sm, Ho and Er; L=N',N",N"',N""-tetramethyl-ethylenediamine; X=Cl, NO_3^-; m=0, 1) are soluble in MeCN, and the compounds[19] $Ln(NCS)_3 \cdot nL$ (Ln=La-Lu; n=3-5; L=2-picoline-N-oxide) are soluble in n-butanol. However, the compounds $[Ln(py)_7(NCMe)][MF_x]_3$ and $[Ln(NMe_3)_4(NCMe)_2][MF_x]_3$ prepared in this work are insoluble. Some possible reasons are proposed below to explain this phenomenon. The process of dissolving a solid in solvent can be discussed according to the energy changes which govern solubility. It can be treated by a simple Born-Haber cycle diagram below (ligands are expressed as L for convenience).

$$[LnL_x][MF_6]_3(s) \xrightarrow{\Delta H_s} [LnL_x]^{3+}(solv.) + 3[MF_6^-](solv.)$$

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$\uparrow -U \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$[LnL_x]^{3+}(g) + 3MF_6^-(g) \xrightarrow{\Delta H_{solv.}(LnL_x^{3+})} \uparrow \qquad\qquad \uparrow$$

$$\uparrow \xrightarrow{3\Delta H_{solv.}(MF_6^-)} \uparrow$$

M=Mo or W

U=lattice energy of $[LnL_x][MF_6]_3$

ΔH_s=enthalpy of solution of $[LnL_x][MF_6]_3$

$\Delta H_{solv.}(LnL_x^{3+})$=enthalpy of solvation of $[LnL_x]^{3+}$

$\Delta H_{solv.}(MF_6^-)$=enthalpy of solvation of MF_6^-

The process of solution is considered as comprising two parts: firstly, the ions in the solid are separated to infinity as gaseous ions, which requires input of the lattice energy, U; and secondly the separated gaseous ions are solvated by the solvent molecules with the evolution of the enthalpy of solvation, $\Delta H_{solv.}$, of the cation and anions. The enthalpy of solution, ΔH_S, is the difference between the lattice energy and the enthalpies of solvation, which determines the probable solubility of the solid. If the energy liberated from the process of solvation, $\Delta H_{solv.}(LnL_x^{3+})$ $+3\Delta H_{solv.}(MF_6^-)$ is greater than the energy necessary to destroy the lattice, U, then, there is enough energy to support the solution of the solid, otherwise, the solution of the solid may be difficult. Although the values of the U, $\Delta H_{solv.}$ and ΔH_S of the complexes $[Ln(py)_7(NCMe)][MF_x]_3$ and $[Ln(NMe_3)_4(NCMe)_2][MF_x]_3$ (Ln=La, Nd or Eu; M=Mo or W; x=6 or 7) are unavailable, they can be qualitatively estimated from the following argument. It is known that in a series of cations having same charge, the smaller the size of the cation is, the greater is its ability to be solvated; thus, the solvation energy of a small cation is greater than that of a large cation. For example, in the alkali metal ions, the order of the ionic radii is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, and the corresponding hydration energies of the cations are 519, 406, 322, 293 and 264 $kJmol^{-1}$ respectively. This results in significant differences in solubility of their ionic salts with a common anion such as ClO_4^-. In this series, the solubility of $LiClO_4$ is greater than that of $NaClO_4$, and the other three are insoluble.[2] The

insoluble compounds, $[Ln(py)_7(NCMe)][MF_6]_3$ and $[Ln(NMe_3)_4(NCMe)_2][MF_6]_3$ (Ln=La, Nd or Eu; M=Mo or W) have a large complex cation since both py and NMe_3 are larger ligands than MeCN. The solvation energies of these cations will be less than for $[Ln(NCMe)_3]^{3+}$ (Ln=La, Nd or Eu), and this results in the decrease of $\Delta H_{solv.}(LnL_x^{3+})$. The insoluble complexes are obtained from mixing solutions of $[Ln(NCMe)_3][MF_x]_3$ in MeCN with py or NMe_3, and they can be regarded as having been prepared in a mixed solvent consisting of MeCN and py or NMe_3. The dielectric constant[135] of py(12.4) is less than that of MeCN(37.5), (the dielectric constant of NMe_3 has not been found in the literature but it is likely small). It is known that the dielectric constants of non-aqueous solvents have an important effect on their power to dissolve ions.[3] The lower the dielectric constant of a solvent is, the less the ability of the solvent to separate ions in solution will be; for example, the general drop in solubilities of the alkali halides from H_2O to SO_2 reflects the drop in dielectric constant from 81 for H_2O to 22 for ammonia and 12 for SO_2.[3] Therefore, it is understandable that a decrease in the dielectric constant of the solvent produces a decrease in solubility of the compounds prepared in this work. What may be a similar situation has been found for the compounds Tl^IUF_6 and $Tl^I(NMe_3)_2UF_6$ by Siddique.[135] The salt Tl^IUF_6 is soluble in MeCN, but when a solution of Tl^IUF_6 in MeCN is mixed with NMe_3, a green precipitate of $Tl^I(NMe_3)_2UF_6$ is formed quickly.

Uranium hexafluoride is reported to be the strongest oxidizing agent of the series considered in this work,[77] however, it is

found that UF_6 does not react with any of the metals used, but rather attacks the solvent. There are reactions between some of the lanthanide metals and MoF_6 or WF_6, but they occur very slowly. This situation has also been found in previous work involving other elements. In order to determine whether there is any overall pattern in reactions between the oxidizing agents and different elements in acetonitrile, details of the reactions involving a number of the elements which have been studied are given in Tables 6.2-6.4. Reactions in Table 6.2 appear to be largely thermodynamically controlled, and the elements in Table 6.2 react readily with the oxidizing agents. They are mostly in either the "IB and IIB" groups or the "p" block of the periodic table. However, as can be seen from Table 6.3, some elements which belong to the "d" block of the periodic table react with MoF_6 or WF_6 with difficulty, and they do not react with UF_6. The cases of the metals Ni, La and Nd are interesting with respect to the factors that affect their oxidation by MF_6 (M=U, Mo or W), in that the apparent oxidizing abilities of UF_6 and MoF_6, which are thermodynamically stronger oxidizing agents than WF_6, appear to be inferior at least in two cases. The hexafluoride, MoF_6, does not react with lanthanum and neodymium metal powders, but it reacts with the pieces of Nd metal ingot freshly cut in the glove box. This suggests that the oxidized film on the surface of the metal inhibits the reaction with MoF_6. Lanthanide metals are very reactive and become easily covered with an oxidized film, protecting them from further oxidation. The known oxide of La is the sesquioxide, La_2O_3. Sesquioxides of the lanthanides generally fall into three different crystal structural types, termed rare earth A, rare earth B and

Table 6.2

Oxidation states of the elements oxidized by both the NO^+ cation and the hexafluorides in acetonitrile

	UF_6	MoF_6	NO^+	WF_6	Ref.
Cu	Cu(II)	Cu(II)	Cu(II)	Cu(I)	76,78
Ag	Ag(I)	Ag(I)	Ag(I)	Ag(I)	76,136
Cd	Cd(II)	Cd(II)	a	Cd(II)	76
Hg	Hg(II)	Hg(II)	a	Hg(I),Hg(II)	76
Tl	Tl(III)	Tl(I), Tl(III)	Tl(I)	Tl(I)	76,135
Te	Te(IV)	Te(IV)	Te(IV) ?	no reaction	153
Br_2	Br(I)	no reaction	no reaction	no reaction	153
I_2	I(I)	I(I)	no reaction	no reaction	112
Fe	a	a	Fe(II)	Fe(II)	154

a : not studied.

Table 6.3

Oxidation states of the elements oxidized slowly by MoF_6 or WF_6 in acetonitrile but not by UF_6

	MoF_6	WF_6	Ref.
Mn	Mn(II)	Mn(II)	76
Co	Co(II)	Co(II)	76,113
Ni	Ni(II) *	Ni(II)	76,113
Zn	Zn(II)	Zn(II)	76,120
Pb	Pb(II)	Pb(II)	76
Au	Au(I)	no reaction	136
Mo	Mo(v)	Mo(v)?	155
W	W(v)	W(v)	155
La	no reaction	La(III)	this work
Nd	Nd(III)*	no reaction	this work
Eu	Eu(III)	Eu(III)	this work

* The massive metals are not oxidized by MoF_6, only metals that are free of oxidized film react.

Table 6.4
The elements oxidized by NO^+ but not (or with difficulty) by the hexafluorides in MeCN

	NO^+ *	MoF_6	WF_6	Ref.
Mn	Mn(II)	Mn(II)	Mn(II)	76,78
Co	Co(II)	Co(II)	Co(II)	76,78
Ni	Ni(II)	Ni(II)	Ni(II)	76,78,113
Au	Au(I)	Au(I)	no	136
La	La(III)	no	La(III)	this work
Nd	Nd(III)	Nd(III)	no	this work,79
Eu	Eu(III)	Eu(III)	Eu(III)	this work
Tm	Tm(III)	no	no	this work

no: no reaction.

* as the PF_6^- or BF_4^- salts.

rare earth C.[156] The oxide La_2O_3 belongs to structure type A. The A form is rather complex and each lanthanum ion has an unusual seven-coordinate environment; six oxygen atoms form an octahedral grouping round the metal, the additional oxygen being added above one face of the octahedron. This kind of structure is very compact, and the bonding between La^{3+} and O^{2-} is strong. The nearest oxygen neighbours of La^{3+} are 3 at 2.38, 1 at 2.45 and 3 at 2.72 Å (Fig. 6.1).[157] The +3 oxidation state is the only stable oxidation state found in the compounds of the metal, hence the formation of an oxide involving an intermediate state; for example, La^{2+} which would facilitate e^- transfer, is not likely to occur. In combination with the strong bonding between La^{3+} and O^{2-} it becomes very difficult for MoF_6 to break the oxidized film framework and react with metallic lanthanum.

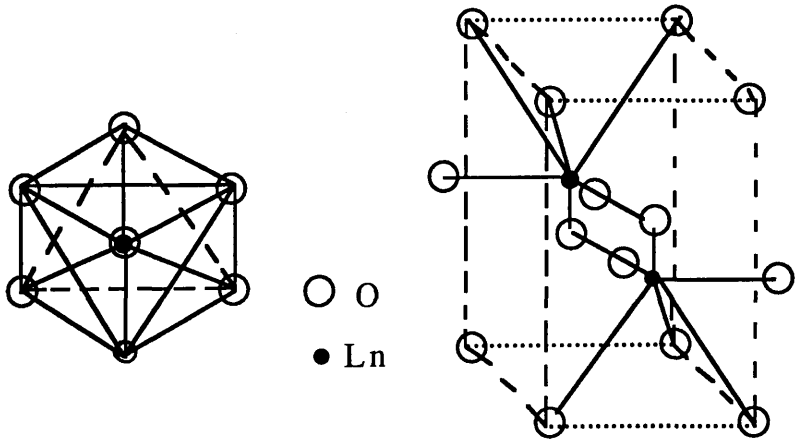


Fig. 6.1 The structure type A of rare earth sesquioxides.[157]

The compound MoF_6 is a stronger oxidizing agent than WF_6[77], but lanthanum metal reacts with WF_6 and does not react with

MoF_6. If the oxide film of the metal inhibits the reaction with MoF_6, why does it not inhibit the reaction with WF_6? It is known that in many cases WF_6 forms the anion WF_7^- readily by a fluoride ion transfer reaction.[77,113,135] A similar situation also occurs in the case of MoF_6,[158] but it appears not to be so widespread. This suggests that WF_6 is a strong Lewis acid, such that it may participate in an interaction with the sesquioxide of lanthanum, forming a Lewis acid-Lewis base adduct, so that the oxide film framework is broken down enabling metallic lanthanum to react with WF_6. A suggested reaction scheme is given below.

$$La_2O_3 + WF_6 \longrightarrow WF_6 \cdot O^{2-} + La^{3+}$$

$$La^{3+} + MeCN \longrightarrow La^{3+}(solv.)$$

$$La^{o}(solv.) + WF_6 \xrightarrow{MeCN} La^{3+}(solv.) + WF_6^- \longrightarrow$$

$$\longrightarrow [La(NCMe)_3][WF_6]_3$$

The adduct $WF_6.O^{2-}$, presumed to be unstable, will decompose to La_2O_3 and WF_6. Insoluble La_2O_3 would be removed by recrystallization of the product. The process of the reaction suggested above is difficult for MoF_6, which does not react with the La or Nd oxides. It is, however, thermodynamically strong enough to react with metallic neodymium.

A similar situation was met with by Prouff.[113] She studied the reactions between massive nickel and MoF_6 or WF_6 and found that WF_6 reacted with massive nickel but MoF_6 did not react. However, chemically cleaned nickel and vacuum evaporated nickel film reacted with MoF_6 to a limited extent. This indicated that an important reason for the inertness of MoF_6 towards some massive metals is the presence of an oxidized film on the surface. It was proposed[113] that the oxides of transition metals can be grouped into two fairly distinct classes: 1) labile oxides which react quickly, e.g. iron oxide; 2) inert oxides which react only slowly, e.g. nickel oxide. In view of this point, it can be understood why many "d" block elements and some "f" block elements do not react with UF_6 and react slowly with MoF_6 or WF_6. In the first case, because UF_6 can react slowly with the solvent,[134] it tends to attack the solvent when a reaction with a metal is inhibited by the oxidized film on the surface of metal. In the second case, because MoF_6 or WF_6 must first break down the oxidized film of the metals and then react with the metal itself, this results in reactions being slow. In some special cases such as Ni, La and Nd, if MoF_6 can not break down the oxidized film framework, no reaction occurs.

The present work has showed that there are significant differences in the behaviour of five NO^+ salts towards the lanthanide metals. The salts $NOUF_6$ and $NOWF_7$ do not react with any of the lanthanide metals used; $NOBF_4$ reacts only with Eu, and $NOMoF_6$ reacts only with Nd; however $NOPF_6$ reacts with all the lanthanide metals used. The NO^+ cation should behave identically in all cases, as the anion and cation are considered to

be well separated in solution. Therefore, the observed behaviour is very difficult to understand. Three possible reasons which may be important in helping to account for differences are the presence of an oxidized film on the surface of the metals; different solubilities of the NO^+ salts in acetonitrile solution, and possible interactions between a Ln(III) cation and a fluoroanion. A number of metals which cannot (or can only with difficulty) be oxidized by the hexafluorides can be oxidized readily by the NO^+ salts. These NO^+ salts are either $NOBF_4$ or $NOPF_6$ (Table 6.4), and they all have the ability to break down the oxidized film on the surface of the metals, as can be seen from Table 6.4. Therefore, for the two NO^+ salts, the differences in behaviour observed towards lanthanide metals are considered to be mainly due to the latter two reasons. From the present work, it is known that the solubilities of $NOPF_6$ and $NOMoF_6$ in MeCN are greater than those of $NOBF_4$, $NOUF_6$ and $NOWF_7$. which possibly results in a difference in the effective concentration of the NO^+ cation in MeCN solution. Thus, $NOBF_4$ can react only with the most reactive metal, Eu, but $NOPF_6$ reacts with all metals used. The second reason may be due to a difference in interaction between the Ln(III) cation and the two different fluoroanions. Perhaps, anion PF_6^- has a slightly stronger ability to interact with the Ln(III) cation than $NOBF_4^-$, thus, $NOPF_6$ reacts easily with lanthanide metals. In the $NOMoF_6$ case, its solubility in MeCN is high, which results in the increase of the effective concentration of the NO^+ in MeCN; thus it reacts with the pieces of Nd metal ingot freshly cut in the glove box. However, the oxidized film on the surface of a metal may play an important role in inhibiting

its reaction with the other metals. The inertness of $NOUF_6$ and $NOWF_7$ towards the metals used is considered to be due mainly to low solubilities of these salts in MeCN and the effect of the oxidized film on the metals.

In conclusion, the present work has showed that the reactions between the lanthanide metals and the hexafluoride oxidizing agents in acetonitrile are similar to those of many other transition metals. Reactions may be inhibited by an oxidized film, especially for UF_6 and MoF_6. The hexafluoride WF_6 has the ability to break down the oxidized film. The interaction of the lanthanide(III) cations and fluoroanions causes a decrease of the apparent coordination numbers of some lanthanide complexes prepared. It is believed that a number of kinetic factors play as important a role as thermodynamic factors in reactions between the hexafluorides or the NO^+ salts and the metals.

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